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

*J. Lu, C. Aydin, N. D. Browning, B. C. Gates**
Imaging Gold Atom Catalytic Sites in Zeolite NaY

F. Liao, Z. Zeng, C. Eley, Q. Lu, X. Hong, S. C. E. Tsang**
Electronic Modulation of a Cu–ZnO Catalyst by Heterojunction Establishment for Selective Hydrogenation of Carbon Dioxide to Methanol

*A. Elahi, T. Fowowe, D. J. Caruana**
Dynamic Electrochemistry in Flame Plasma Electrolyte

*M. Kessler, S. Schüler, D. Hollmann, M. Klahn, T. Beweries, A. Spannenberg, A. Brückner, U. Rosenthal**
Photoassisted Ti–O Activation in a Decamethyltitanocene Dihydroxo Complex: Insights into the Elemental Steps of Water Splitting

J. Graton, Z. Wang, A.-M. Brossard, D. G. Monteiro, J.-Y. Questel, B. Linclau**
An Unexpected and Significantly Lower Hydrogen-Bond Donating Capacity of Fluorohydrins Relative to Nonfluorinated Alcohols

*T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing**
Positive at Last: $[P_9]^+[Al(OR^F)_4]^-$, the First Pure Phosphorus Cation Salt

*J. Quinton, S. Kolodych, M. Chaumonet, V. Bevilacqua, M.-C. Nevers, H. Volland, S. Gabillet, P. Thuéry, C. Créminon, F. Taran**
Reaction Discovery Using Sandwich Immunoassay

Author Profile

"A good work day begins now and again with the thought "Time is a strange thing" (from 'Der Rosenkavalier'). My secret/not-so-secret passion is a deep curiosity for people. …"
This and more about Helmut Schwarz can be found on page 5532.

News

E. W. Meijer

D. A. Tirrell

H. Ringsdorf

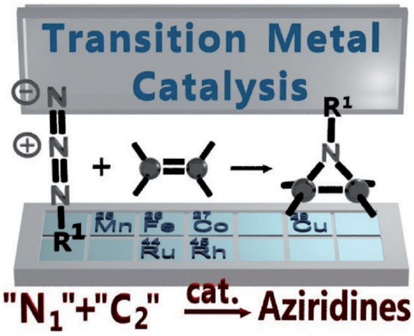
Books

Highlights

Aziridine Synthesis

N. Jung, S. Bräse* ________ **5538 – 5540**

New Catalysts for the Transition-Metal-Catalyzed Synthesis of Aziridines

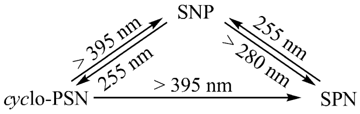


$C_2 + N_1$: The transition-metal-catalyzed reaction of alkenes with azides is an important tool for the formation of aziridines. Besides many recently published ruthenium, copper, and manganese catalysts, a novel macrocyclic tetracarbene iron(II) catalyst promotes the synthesis of aziridines in good yields and with low catalyst loadings.

Reactive Intermediates

H.-J. Himmel,* G. Linti ____ **5541 – 5542**

OPN and SPN: Small Molecules with Great Potential



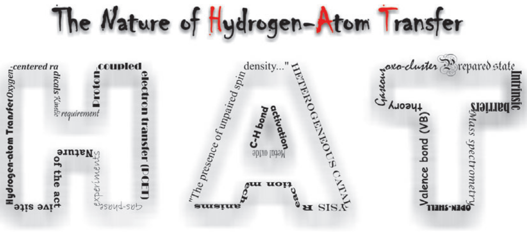
Small but impressive: Since triatomic, highly reactive molecules, such as OPN, SPN (see scheme), and SiS_2 have special electronic properties, they are expected to display rich and diverse reactivity. Matrix-isolation studies together with quantum chemical studies now form a solid basis for future preparative work.

Minireviews

Hydrogen-Atom Transfer

N. Dietl, M. Schlangen,
H. Schwarz* ______________ **5544 – 5555**

Thermal Hydrogen-Atom Transfer from Methane: The Role of Radicals and Spin States in Oxo-Cluster Chemistry



The need for spin: Owing to its importance for numerous chemical processes, the nature of hydrogen-atom transfer (HAT) has become a major area of research. This Minireview shows the intrinsic requirements that enable gaseous oxo clusters to bring about HAT reactivity from saturated hydrocarbons at room temperature, thus revealing the crucial role of unpaired spin density at the abstracting atom.

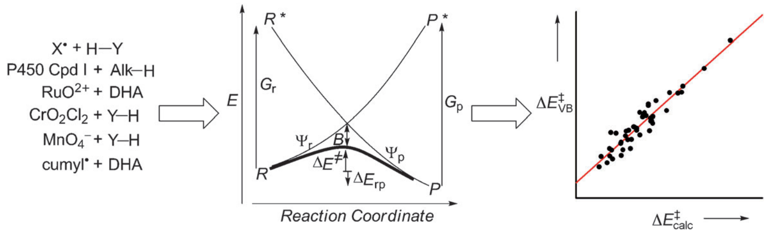
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Reviews

Valence Bond Diagrams

W. Lai, C. Li, H. Chen,
S. Shaik* ______ 5556 – 5578

Hydrogen-Abstraction Reactivity Patterns from A to Y: The Valence Bond Way



Give us insight and good numbers: Is it possible to understand one of the fundamental reactions in nature, the hydrogen-atom transfer (HAT), using a single unifying theory? The valence bond diagram model is such a unifying theory. It enables the barriers to be estimated from raw data (see plot), thereby creating a natural bridge to the Marcus equation, addresses the relationships between HAT to proton-coupled electron transfer (PCET), and shows how H-abstractions by closed-shell molecules can occur.

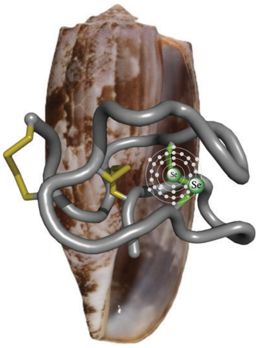
Communications

Protein Folding

A. M. Steiner, K. J. Woycechowsky,
B. M. Olivera, G. Bulaj* ______ 5580 – 5584

Reagentless Oxidative Folding of Disulfide-Rich Peptides Catalyzed by an Intramolecular Diselenide

Frontispiece



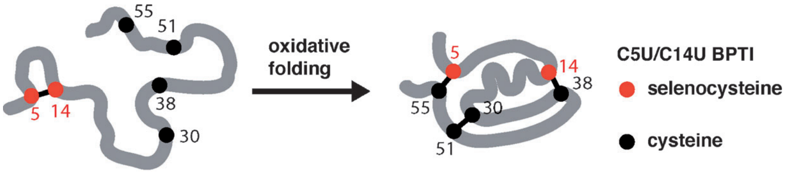
Building bridges: In cysteine-rich peptides, diselenides can be used as a proxy for disulfide bridges as the energetic preference for Se–Se bonds over mixed Se–S bonds simplifies folding (see picture). An intramolecular diselenide bond efficiently catalyzes the oxidative folding of selenopeptide analogues of conotoxins, and serves as a reagentless method to accelerate formation of various native disulfide bridging patterns.

Protein Folding

VIP

N. Metanis, D. Hilvert* ______ 5585 – 5588

Strategic Use of Non-Native Diselenide Bridges to Steer Oxidative Protein Folding



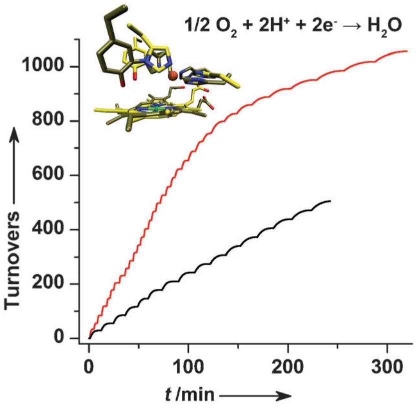
Targeted insertion of a non-native diselenide cross-link into a cysteine-rich protein can be exploited to direct the early stages of oxidative folding so as to avoid accumulation of unproductive intermediates that limit folding efficiency. This simple strategy could facilitate the production of many difficult-to-fold peptides and proteins.

Enzyme Design

K. D. Miner, A. Mukherjee, Y.-G. Gao, E. L. Null, I. D. Petrik, X. Zhao, N. Yeung, H. Robinson, Y. Lu* ——— **5589 – 5592**

A Designed Functional Metalloenzyme that Reduces O_2 to H_2O with Over One Thousand Turnovers

No spare Tyr: Rational design of functional enzymes with a high number of turnovers is a challenge, especially those with a complex active site, such as respiratory oxidases. Introducing two His and one Tyr residues into myoglobin resulted in enzymes that reduce O_2 to H_2O with more than 1000 turnovers (red line, see scheme) and minimal release of reactive oxygen species. The positioning of the Tyr residue is critical for activity.

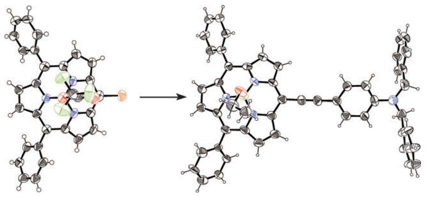


Porphyrinoids

M. Kitano, S. Hayashi, T. Tanaka, H. Yorimitsu, N. Aratani, A. Osuka* ——— **5593 – 5597**

Effective meso Fabrications of Subporphyrins

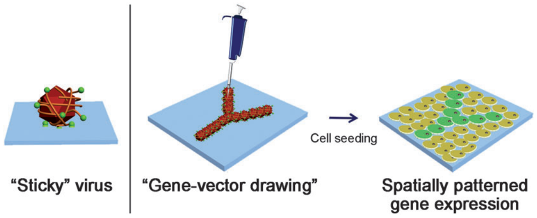
A meso-free subporphyrin was prepared and quantitatively converted into meso-brominated subporphyrin, which is an effective precursor for the facile installation of substituents at the meso position. The meso-(4-amino)phenylethynyl subporphyrins (see picture; N blue, O red, Br orange, F pale green, B dark green) and a butadiyne-bridged dimer have split Soret-like bands and red-shifted and intensified fluorescence.



Gene Expression

E. Kim, I. T. Song, S. Lee, J. S. Kim, H. Lee,* J. H. Jang* ——— **5598 – 5601**

Drawing Sticky Adeno-Associated Viruses on Surfaces for Spatially Patterned Gene Expression



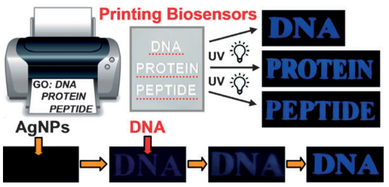
Sticky stuff: A versatile strategy to spatially control gene expressions of mammalian cells is developed. A catecholamine polymer (PEI-C) is used to functionalize surfaces of adeno-associated viruses (AAV). Because of the underwater adhesive property of catechol, AAV/PEI-C hybrid vectors become highly "sticky", resulting in spatially patterned viral attachment onto substrates by the simple "gene-vector drawing" technique (see picture).

Graphene Oxide Biosensors

Q. Mei, Z. Zhang* ——— **5602 – 5606**

Photoluminescent Graphene Oxide Ink to Print Sensors onto Microporous Membranes for Versatile Visualization Bioassays

Read all about it: Graphene oxide (GO) sensors can be formed on microporous membranes for the visual detection of peptides, protein, and DNA. Silver nanoparticles (AgNPs) modified with ligands, antibodies, and oligonucleotides adsorb onto the surface of GO nanosheets and quench the fluorescence. Upon addition of analytes, the AgNPs disassociate from the nanosheets, and thus the fluorescence is immediately restored.



Career in Blood gas Analytics

Who we are

At Roche, 80,000 people across 150 countries are pushing back the frontiers of healthcare. Working together, we've become one of the world's leading research-focused healthcare groups. Our success is built on innovation, curiosity and diversity, and on seeing each other's differences as an advantage. To innovate healthcare, Roche has ambitious plans to keep learning and growing – and is seeking people who have the same goals for themselves.

The Position

For our newly created Blood gas analytics organization within the Global Platform and Supports department, we are looking for highly motivated and communicative Senior Engineers.

Current open positions are/include:

- Unit Project Leader
- Senior Development Engineer Sensors
- Senior Engineer Polymer and Materials Chemistry

Who you are

You're open for new ideas and are able to break away from the usual thought patterns. You're someone who wants to influence your own development. You're looking for a company where you have the opportunity to pursue your interests across functions and geographies, and where a job title is not considered the final definition of who you are, but the starting point.

For this challenging job opportunities the following skills are required: Master's degree in Chemistry (Electrochemistry) or equivalent degree in natural science

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Contact: R. Wallimann, Recruiting Specialist
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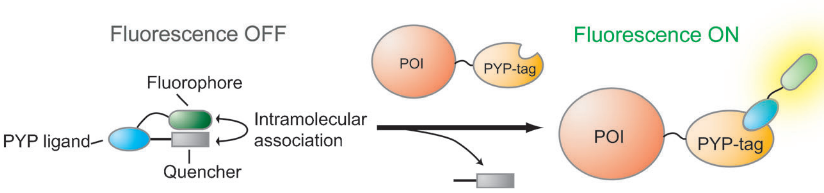
Analyzing Works of Art

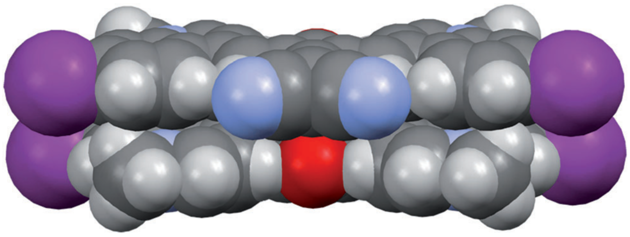
In situ analysis: Near infrared imaging spectroscopy (1000–2500 nm) is used to map the use of a fat-containing paint binder, likely egg yolk, in situ on a work of art for the first time. The identification of the use of egg tempera on a 15th century illuminated manuscript leaf (*Praying Prophet* by Lorenzo Monaco) sheds light on the relationship between painters and illuminators and can inform preservation decisions.

Fluorescent Probes



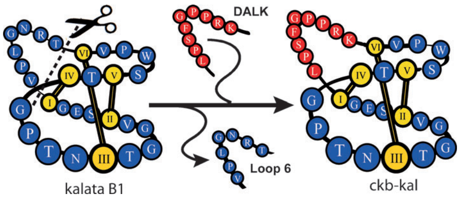
Turn on the switch: Fluorogenic probes for protein labeling based on the photoactive yellow protein (PYP) tag were developed. The fluorescence of the probes is turned off by intramolecular association and switched on by the reversal of this interaction upon reaction with the PYP tag that is fused to the protein of interest (POI, see scheme). The rapid and specific labeling reaction enabled the imaging of cell-surface proteins without washing.

Supramolecular Chemistry

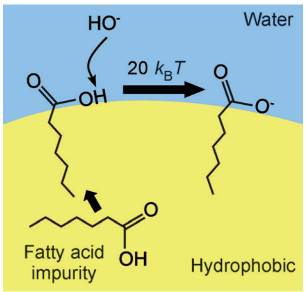


The “dye” is cast: An isodesmic self-assembly process of near-infared-absorbing, acceptor-substituted squaraine dyes, assisted by halogen–halogen and halogen–arene interactions, is observed in toluene. The aggregation process was monitored by UV/Vis/NIR absorption and NMR experiments, thus providing insight into the structural features (see figure; O red, I violet, N blue) as well as the binding strengths of the formed aggregates.

Peptide Therapeutics



Edible: By grafting natural peptide antagonists onto the cyclotide kalata B1, orally active peptides were engineered, which are potentially useful therapeutics for the treatment of inflammatory pain. For example, the entire loop 6 of kalata B1 was replaced with the peptidic bradykinin B_1 receptor antagonist DALK (red in scheme) to obtain the cyclic bradykinin antagonist ckb-kal.



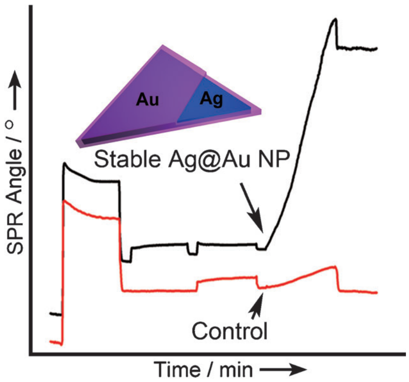
Impure at heart: A pH-dependent negative charge of the interface between a hydrophobic phase and water results from the reaction of hydroxide ions with traces of fatty acids, contained in the hydrophobic phase (see scheme). This reaction explains the uptake of hydroxide ions by the interface with a large free energy change.

Interfacial Charge

K. Roger,* B. Cabane ______ **5625 – 5628**

Why Are Hydrophobic/Water Interfaces Negatively Charged?

An SPR biosensor was developed by employing highly stable Au-protected Ag nanoplates (NP) as enhancers (see picture). Superior performance was achieved by depositing a thin and uniform coating of Au on the Ag surface while minimizing disruptive galvanic replacement and retaining the strong surface plasmon resonance (SPR) of the silver nanoplates.

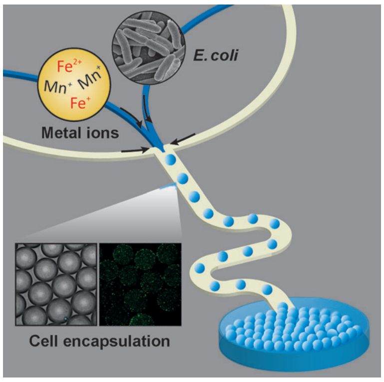


Plasmonic Nanosensors

C. Gao, Z. Lu, Y. Liu, Q. Zhang, M. Chi, Q. Cheng, Y. Yin* ______ **5629 – 5633**

Highly Stable Silver Nanoplates for Surface Plasmon Resonance Biosensing

All under control: A microfluidic droplet generator uniformly encapsulates an equivalent number of engineered *E. coli* cells and the same Fe and Mn metal ion concentrations in identically sized droplets. The synthesized biogenic FeMn paramagnetic nanoparticles inside the cells are eco-friendly and cost-effective.

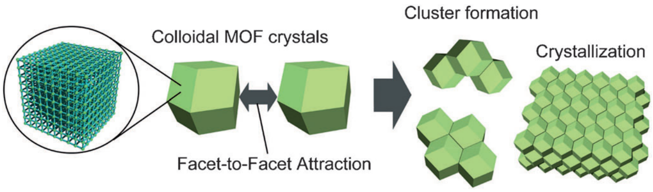


Biogenic Nanoparticles

J. H. Jung, T. J. Park, S. Y. Lee,* T. S. Seo* ______ **5634 – 5637**

Homogeneous Biogenic Paramagnetic Nanoparticle Synthesis Based on a Microfluidic Droplet Generator

Back Cover



MOFs get attraction: Supraparticle self-assembly of a colloidal metal–organic framework (MOF) is achieved through simple capillary and van der Waals attractions. When suspensions of MOF particles are allowed to evaporate, hexagonal packings with controlled crystal orientation result (see scheme). The self-assembly can be visualized at the single-particle level.

Supraparticles

N. Yanai, S. Granick* ______ **5638 – 5641**

Directional Self-Assembly of a Colloidal Metal–Organic Framework

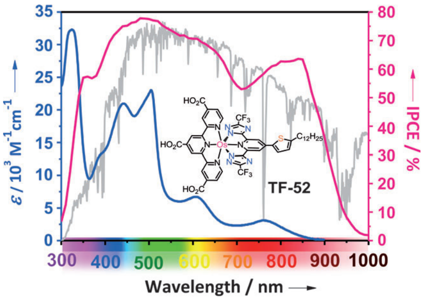
Inside Back Cover

Solar Cells

K.-L. Wu, S.-T. Ho, C.-C. Chou, Y.-C. Chang, H.-A. Pan, Y. Chi,* P.-T. Chou* ______ **5642 – 5646**

Engineering of Osmium(II)-Based Light Absorbers for Dye-Sensitized Solar Cells

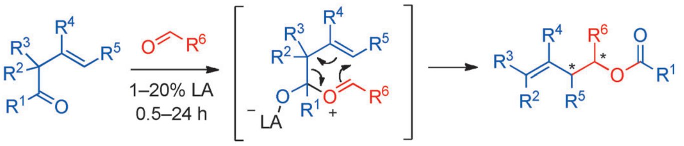
Panchromatic Os^{II} sensitizers for dye-sensitized solar cells (DSCs) were prepared. A DSC based on **TF-52** (see picture) showed promising performance characteristics: short-circuit photocurrent density $J_{SC} = 23.3\ \mathrm{mA\,cm^{-2}}$, open-circuit photovoltage $V_{OC} = 600$ mV, fill factor (FF) = 0.633, and power conversion efficiency $\eta = 8.85\,\%$ under AM 1.5G simulated one-sun irradiation.



Synthetic Methods

Y. Zou, C. Ding, L. Zhou, Z. Li, Q. Wang,* F. Schoenebeck, A. Goeke* ______ **5647 – 5651**

Tandem Cross-Dimerisation/Oxonia-Cope Reaction of Carbonyl Compounds to Homoallylic Esters and Lactones

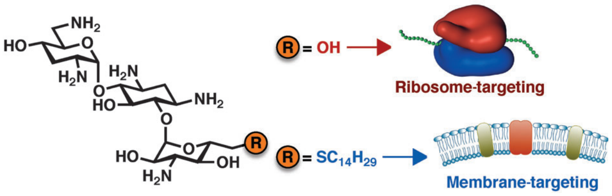


Conceptually different: This allyltransfer reaction is catalyzed by Lewis acids (LAs) and proceeds atom-economically by disproportionation of the carbonyl groups through organized oxonia-Cope transition states (see scheme). A stereoselective [$n+4$] ring enlargement leads to a variety of macrolides with 9- to 16-membered rings.

Antibiotics

I. M. Herzog, K. D. Green, Y. Berkov-Zrihen, M. Feldman, R. R. Vidavski, A. Eldar-Boock, R. Satchi-Fainaro, A. Eldar, S. Garneau-Tsodikova,* M. Fridman* ______ **5652 – 5656**

6′′-Thioether Tobramycin Analogues: Towards Selective Targeting of Bacterial Membranes



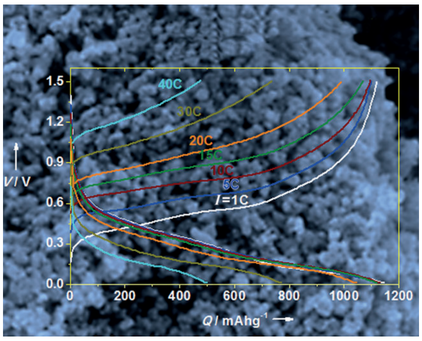
Amphiphilic tobramycin analogues with potent antibacterial activity against tobramycin-resistant bacteria were synthesized. Most analogues were found to be less prone to deactivation by aminoglycoside-modifying enzymes than tobramycin. These compounds target the bacterial membrane rather than the ribosome (see picture). The lipophilic residue of these analogues is key to their antibacterial potency and selectivity towards bacterial membranes.

Inside Cover

Electrochemistry

K. H. Seng, M. Park, Z. P. Guo,* H. K. Liu, J. Cho* ______ **5657 – 5661**

Self-Assembled Germanium/Carbon Nanostructures as High-Power Anode Material for the Lithium-Ion Battery

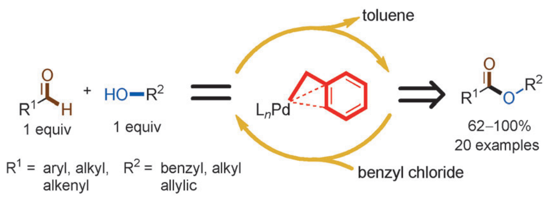


Simple and powerful: Two germanium/carbon nanostructures were synthesized through a facile self-assembly method. Controlling the size of the precursor germanium nanoparticles produces cluster and non-clustered nanostructures. The cluster-Ge/C sample showed better capacity retention and an exceptionally high rate performance (see picture; Q = charge capacity and V = voltage).

Synthetic Methods

C. Liu, S. Tang, L. Zheng, D. Liu, H. Zhang, A. Lei* ________ 5662 – 5666

Covalently Bound Benzyl Ligand Promotes Selective Palladium-Catalyzed Oxidative Esterification of Aldehydes with Alcohols

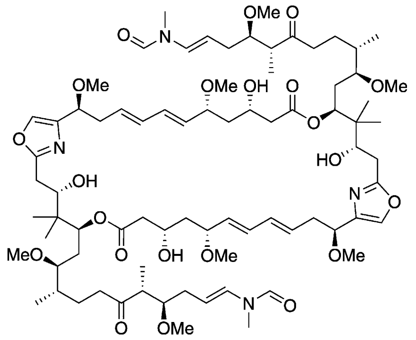


It's a benzyl kind of magic: In the title reaction proceeding with benzyl chloride as the oxidant, the benzyl group serves as a carbon ligand, thus having an η^3-coordination effect on palladium (see scheme). A variety of aldehydes and alcohols were selectively converted into the corresponding esters in good to excellent yields.

Natural Products Synthesis

M. Dieckmann, M. Kretschmer, P. Li, S. Rudolph, D. Herkommer, D. Menche* ________ 5667 – 5670

Total Synthesis of Rhizopodin

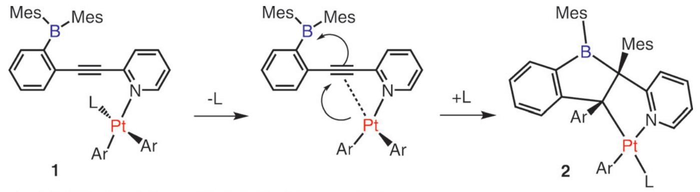


Symmetry helps: The total synthesis of the potent actin-targeting C_2-symmetric myxobacterial macrolide rhizopodin (see scheme) is accomplished by the convergent assembly of three building blocks of similar complexity, a concise macrocyclization strategy, and a late-stage introduction of the labile side chains.

Cascade Cyclization

C. Sun, Z. M. Hudson, L. D. Chen, S. Wang* ________ 5671 – 5674

Double Cyclization/Aryl Migration Across an Alkyne Bond Enabled by Organoboryl and Diarylplatinum Groups



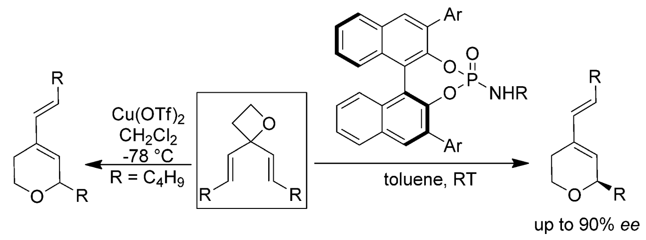
L = DMSO, Ar = Ph or *p*-MeOC$_6$H$_4$, Mes=mesityl

Synergy between metals: Diarylacetylenes **1**, containing both a boryl (BMes$_2$) group and a diarylplatinum group, undergo a transformation involving a double metallocyclization/aryl migration to give tetracycles **2** in high diastereoselectivity (see scheme). This remarkable transformation is enabled by the synergistic interplay of the boryl and the diarylplatinum group.

Synthetic Methods

B. Guo, G. Schwarzwalder, J. T. Njardarson* ________ 5675 – 5678

Catalytic Ring Expansion of Vinyl Oxetanes: Asymmetric Synthesis of Dihydropyrans Using Chiral Counterion Catalysis

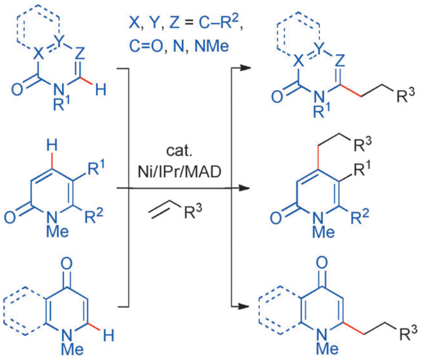


Acid Showdown! The first catalytic ring expansion of vinyl oxetanes to 3,6-dihydro-2*H*-pyrans is described. Copper(II) triflate emerged as the best catalyst for this new transformation, which has broad scope as demonstrated by the eighteen examples included. The symmetric vinyl oxetane substrate can be asymmetrically desymmetrized when using either chiral Lewis or Brønsted acids as catalysts.

C–H Activation

R. Tamura, Y. Yamada, Y. Nakao,*
T. Hiyama* ________ 5679 – 5682

Alkylation of Pyridone Derivatives By Nickel/Lewis Acid Catalysis

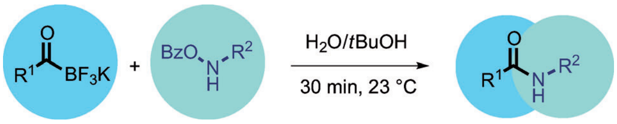


MAD as an additive: The $[Ni(cod)_2]$, $(2,6\text{-}tBu_2\text{-}4\text{-}MeC_6H_2O)_2AlMe$ (MAD), and N-heterocyclic carbene (NHC) catalytic system effected a highly regioselective alkylation of pyridone derivatives (see scheme). Substituted pyridones and related heterocycles react with both terminal and internal alkenes to selectively give a range of nitrogen-containing heterocycles with linear alkyl substituents.

Amide Ligation

A. M. Dumas, G. A. Molander,
J. W. Bode* ________ 5683 – 5686

Amide-Forming Ligation of Acyltrifluoroborates and Hydroxylamines in Water



Come together, right now: Acyltrifluoroborates and *O*-benzoyl hydroxylamines come together to form amides in water (see scheme). The ligations are complete within minutes at room temperature and do not require any reagents or catalysts. The reaction has a broad substrate scope and tolerates unprotected functional groups.

DOI: 10.1002/anie.201203192

50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

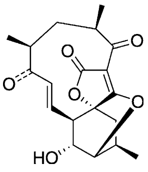
Ferrocene was first reported over 60 years ago (see the forthcoming Essay by H. Werner, *Angew. Chem. Int. Ed.*, in press), and by 1962, the chemistry of π complexes of aromatic compounds with transition metals was sufficiently mature that a Review on the subject was written by K. Plesske, who discussed the aromatic substitution reactions that these systems could undergo. Organometallic chemistry was also the subject of a Communication by W. H. Stubbs and P. L. Paulson, the latter of whom originally synthesized ferrocene, who reported on cyclopentadienyl metal isonitriles of manganese, iron, and nickel.

Organic ring systems with adamantane-type structures were the subject of a Review and a Communication by H. Stetter. In the Review, ring systems such as oxa- and thia-adamantanes, as well as boric acid and metal complexes, were discussed, and results on the fragmentation of 3-bromoadamantane-1-carboxylic acid were reported in the Communication.

The smells of onions and garlic are known to come from sulfur-containing compounds. In a Review, A. I. Virtanen summarized some of the organic sulfur compounds that can be isolated from onions and garlic, including the alkyl sulfide allicin from garlic, and the S-alkenyl-cysteine-S-oxide that is the precursor of the lachrymatory factor in onions. These active substances are formed only when the plant is crushed as the precursors and the enzymes that react with them are located in different cells.

Read more in Issue 6/1962

Rolling in the deep: An enantioselective synthesis of a marine antibiotic (−)-atrop-abyssomicin C (see scheme) is described. The key steps of the synthetic sequence are the application of dual catalysis in the formation of the cyclohexane core, the gold-catalyzed formation of a tricyclic spirotetronate unit, and a highly efficient eleven-membered ring closure by a Nozaki–Hiyama–Kishi reaction.

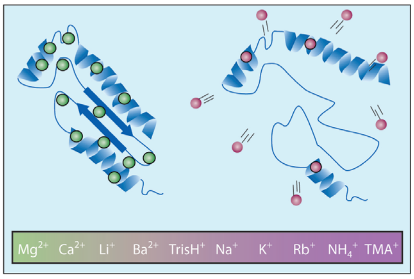


Natural Product Synthesis

F. Bihelovic,* R. N. Saicic* **5687 – 5691**

Total Synthesis of (−)-atrop-Abyssomicin C

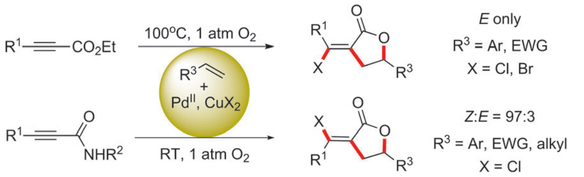
Positively a gas: Protein structure determination using mass spectrometry can be assisted by the addition of stabilizing cations to the gas-phase molecule. Densely charged cations (see scheme, green) are found to stabilize protein tertiary structure for accurate mass determination of homo- or heterogeneous protein complexes. The cations remain tightly bound to the protein throughout the analysis, allowing the protein to remain in a folded state.



Protein Structure

L. Han, S.-J. Hyung,
B. T. Ruotolo* **5692 – 5695**

Bound Cations Significantly Stabilize the Structure of Multiprotein Complexes in the Gas Phase



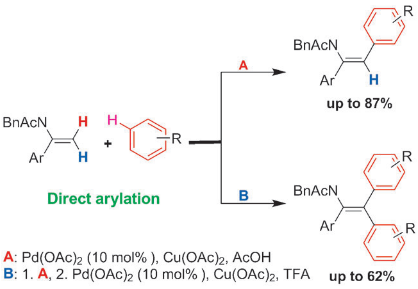
Three in one: A highly efficient and mild Pd^{II}-catalyzed carboesterification of alkenes with carboxylic alkyne derivatives proceeds through a domino-type alkyne–alkene coupling/C–O-bond formation (see scheme). The stereoselectivity is controlled by the choice of substrates and temperature. The reaction provides a convenient method for the construction of naturally occurring biologically active compounds with α-methylene-γ-lactone skeletons.

Synthetic Methods

L. B. Huang, Q. Wang, X. H. Liu,
H. F. Jiang* **5696 – 5700**

Switch of Selectivity in the Synthesis of α-Methylene-γ-Lactones: Palladium-Catalyzed Intermolecular Carboesterification of Alkenes with Alkynes

***Z* only**: An atom-economical synthetic route towards arylated *Z*-enamides through double C–H functionalization is described. The *Z*/*E* selectivity of the palladium-catalyzed monoarylation is absolute (step A in scheme), and the molecular complexity of the products can be further endowed by a sequential second arylation, which requires the use of trifluoracetic acid (TFA; step B).



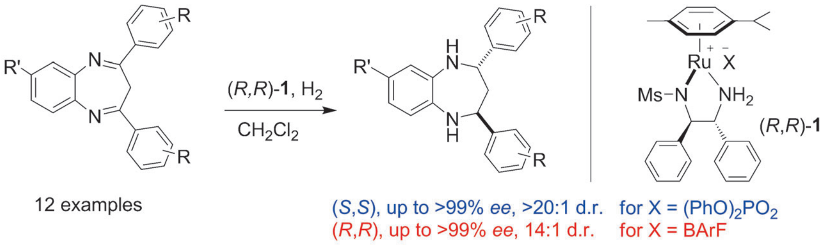
A: $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$, AcOH
B: 1. A, 2. $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$, TFA

C–H Arylation

S. Pankajakshan, Y. H. Xu, J. K. Cheng,
M. T. Low, T. P. Loh* **5701 – 5705**

Palladium-Catalyzed Direct C–H Arylation of Enamides with Simple Arenes

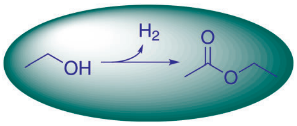
Asymmetric Hydrogenation



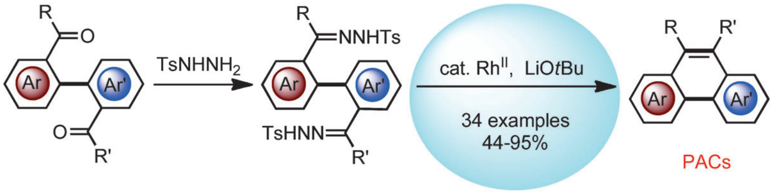
BArFing it out the other way: A highly enantioselective hydrogenation of 2,4-disubstituted 1,5-benzodiazepines using chiral cationic ruthenium diamine catalysts (*R*,*R*)-**1** has been developed (see scheme; BArF = tetrakis(3,5-bistrifluoromethylphenyl)borate). Either enantiomer of 2,4-diaryl-2,3,4,5-tetrahydro-1*H*-benzodiazepine derivatives could be obtained by using the same enantiomer of ligand but in the presence of a different achiral counteranion.

Homogeneous Catalysis

Green is a go: An efficient acceptorless dehydrogenative dimerization of ethanol to give ethyl acetate was realized (see scheme). The reaction proceeds under mild reaction conditions in the presence of a ruthenium catalyst with concomitant liberation of molecular hydrogen, which can be used as a valuable product itself. At low catalyst loading (50 ppm), high yields of ethyl acetate and excellent catalyst turnover numbers are achieved.

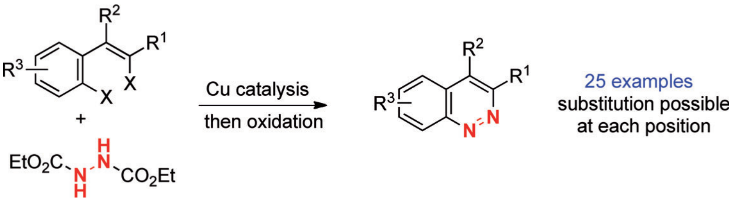


Synthetic Methods



Ahead of the PAC: Polycyclic aromatic compounds (PACs) can be easily accessed by the combination of Suzuki–Miyaura cross-coupling and a [$Rh_2(OAc)_4$]-catalyzed carbene reaction using easily available bis(*N*-tosylhydrazone)s as intermediates (see scheme; Ts = 4-toluenesulfonyl).

Heterocycle Synthesis

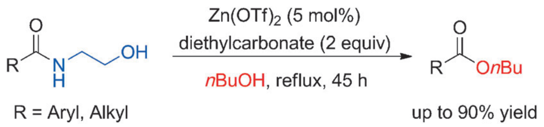


Cinn-tillating synthesis: The combination of a readily available copper catalyst, a simple hydrazide nucleophile, and established difunctionalized building blocks provides a new, flexible route to an underdeveloped class of aromatic heterocycles, cinnolines (see scheme).

Amide Cleavage

Y. Kita, Y. Nishii, T. Higuchi,
K. Mashima* 5723 – 5726

Zinc-Catalyzed Amide Cleavage and Esterification of β-Hydroxyethylamides

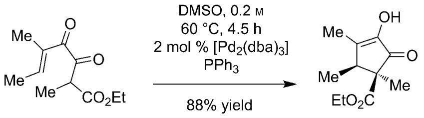


Snipping tool: Zn(OTf)$_2$ is an efficient catalyst for selective cleavage of amides bearing a β-hydroxyethyl group on the nitrogen atom. The mechanism involves an N,O-acyl rearrangement and transesterification. This new catalytic system can be applied to sequence-specific peptide bond scission at the amine side of a serine residue. Tf = trifluoromethanesulfonyl.

Palladium Catalysis

N. Shimada, C. Stewart, W. F. Bow, A. Jolit,
K. Wong, Z. Zhou,
M. A. Tius* 5727 – 5729

Neutral Nazarov-Type Cyclization Catalyzed by Palladium(0)

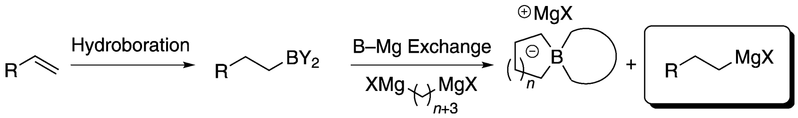


Joining the circle: The first Pd^0 catalyzed Nazarov-type cyclization of diketoesters (see scheme) proceeds in 70% to 95% yield under strictly neutral pH conditions. Aryl substitution of the diketoesters is not required, so the reaction shows great versatility and can also proceed with aliphatic substrates.

Synthetic Methods

M. A. Reichle, B. Breit* 5730 – 5734

Preparation of Alkylmagnesium Reagents from Alkenes through Hydroboration and Boron–Magnesium Exchange



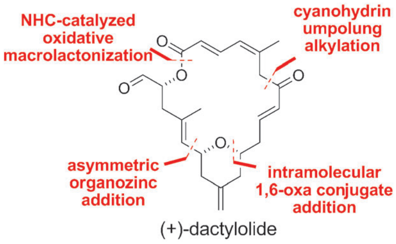
Tolerant: Alkylmagnesium reagents can be synthesized from alkenes through a sequence of hydroboration and subsequent boron–magnesium exchange using a method that tolerates different functional groups (see scheme). The resulting alkylmagnesium reagents can be used in carbon–carbon bond forming reactions, such as alkylation reactions or transition-metal-catalyzed cross-coupling reactions.

Natural Products

K. Lee, H. Kim,* J. Hong* 5735 – 5738

N-Heterocyclic Carbene Catalyzed Oxidative Macrolactonization: Total Synthesis of (+)-Dactylolide

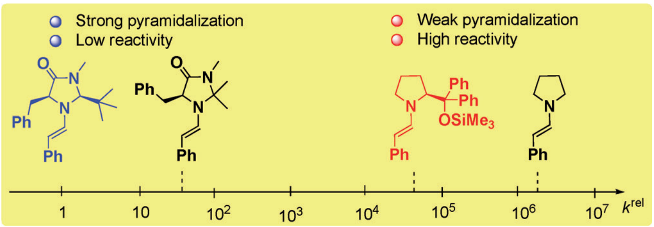
Three key steps constitute the total synthesis of (+)-dactylolide: the 1,6-oxa conjugate addition reaction of a 2,4-dienal for the facile synthesis of the 2,6-*cis*-2-(4-oxo-2-butenyl)tetrahydropyran subunit, the umpolung alkylation reaction of a cyanohydrin, and the NHC-catalyzed oxidative macrolactonization reaction for the synthesis of the 20-membered macrocycle. NHC = N-heterocyclic carbene.



Organocatalysis

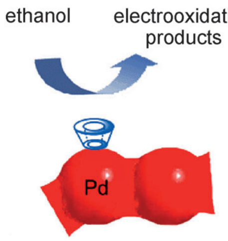
S. Lakhdar,* B. Maji,
H. Mayr* 5739 – 5742

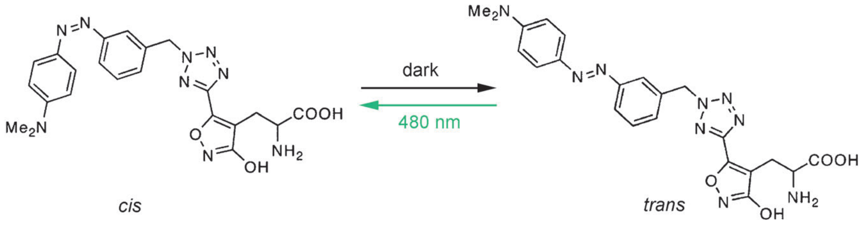
Imidazolidinone-Derived Enamines: Nucleophiles with Low Reactivity



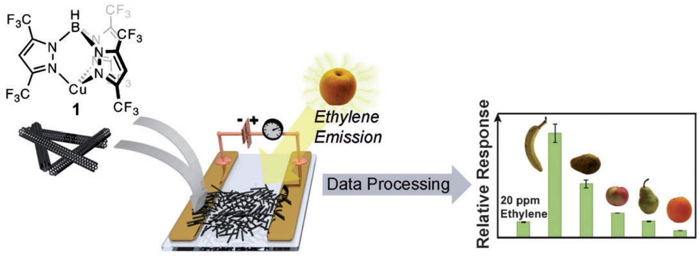
Extraordinarily weak nucleophiles: Enamines derived from imidazolidinones are 10^3–10^5 times less reactive than those derived from the Hayashi–Jørgensen catalyst. This finding explains the lower activity of MacMillan catalysts for enamine-activated reactions.

Nanostructures as catalysts: Pd aerogels modified with α-, β-, and γ-cyclodextrins can be obtained by the spontaneous self-assembly of in situ generated Pd nanoparticles. The Pd aerogels show excellent electrocatalytic activity for the oxidation of ethanol. The catalytic activity is believed to arise from the nonsupported nanometer-scale structure of the aerogel network and the interactions of ethanol with the cyclodextrin.

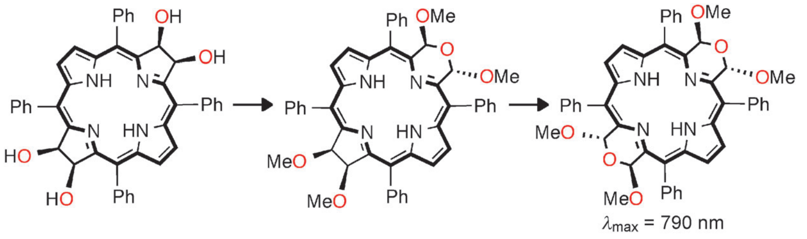




Light switch: A photochromic agonist ATA-3 (see scheme) of AMPA receptors, arguably the most important class of ionotropic glutamate receptors, is shown to be subtype selective, activates the AMPA receptor GluA2 in the dark, and is quickly turned off when irradiated with blue–green light. It can be used to effectively control neuronal activity in the mammalian brain.



Comparing apples and oranges: A chemoresistive sensor for ethylene can be obtained simply by mixing copper complex **1** with single-walled carbon nanotubes. The resulting devices show sub-ppm sensitivity and high selectivity towards ethylene. The utility of the sensor was demonstrated by following ripening stages in different fruits.



Ruffled rings: Both pyrrolidine moieties in *meso*-tetraaryl-7,8,17,18-tetrahydroxybacteriochlorins can be sequentially expanded into morpholine rings to give the first bacteriochlorin-like derivatives containing two non-pyrrolic heterocycles. These porphyrioids are characterized by nonplanar conformations and significantly red-shifted optical spectra, both of which can be modulated by the introduction of linkages between β and *o*-phenyl positions.

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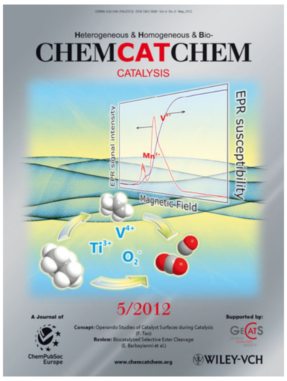

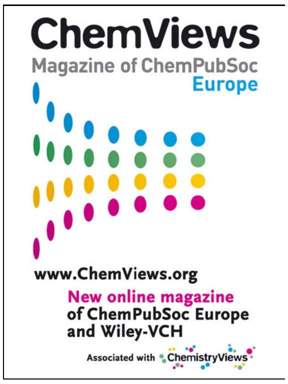

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