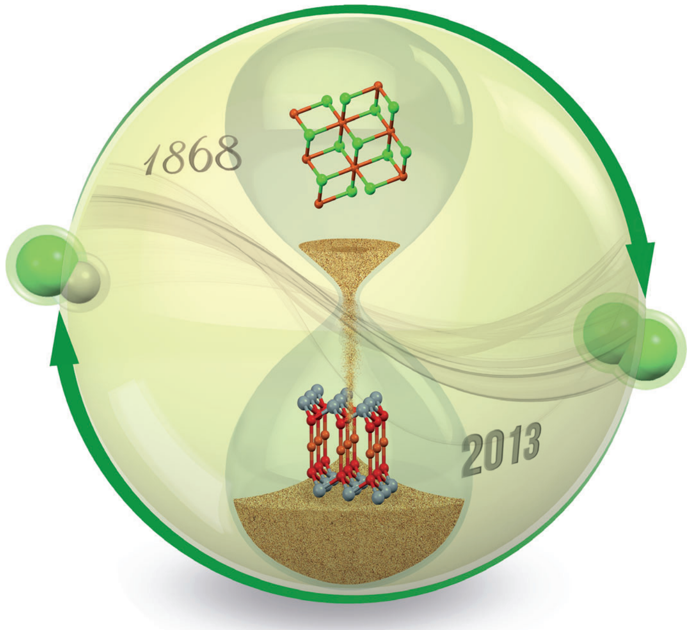
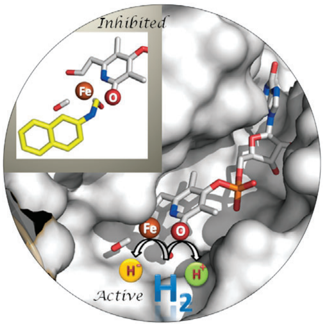
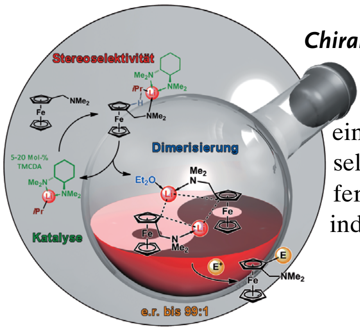
# Seit der Entdeckung Henry Deacons 1868, …



… dass $CuCl_2$ die HCl-Oxidation katalysiert, wurden keine brauchbaren Alternativen zu diesem Katalysator gefunden. Die Gründe dafür sind die Bildung flüchtiger Phasen unter den Reaktionsbedingungen und große Metallverluste. In der Zuschrift auf S. 9954 ff. berichten nun J. Pérez-Ramírez et al. über ihre jüngste Entdeckung, nämlich dass $CuCrO_2$-Delafossit stabil ist unter Chlorierungsbedingungen und in oxidierenden Atmosphären.

**Metalloproteinstrukturen**
[Fe]-Hydrogenase katalysiert die $H_2$-Spaltung und Hydridübertragung auf das Substrat mithilfe des Cofaktors FeGP. In ihrer Zuschrift auf S. 9838 ff. stellen S. Shima et al. die Struktur eines Isocyanid-Komplexes der [Fe]-Hydrogenase vor.





**Chirale Metallocene**
In ihrer Zuschrift auf S. 10019 ff. zeigen C. Strohmann et al., dass katalytische Mengen eines chiralen Additivs ausreichen, um die stereoselektive *ortho*-Lithiierung von *N*,*N*-Dimethylferrocenylmethylamin durch 2-Propyllithium zu induzieren.

**Poröse Polymere**
X. Feng et al. berichten in der Zuschrift auf S. 9850 ff. über die graphenvermittelte Synthese von schichtförmigen konjugierten mikroporösen Polymeren, die durch Erhitzen in poröse Kohlenstoffmaterialien umgewandelt werden können.

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Marion Schulz
*E-Mail:* mschulz@wiley-vch.de
jspiess@wiley-vch.de
*Telefax:* (+49) 6201–606-550
*Telefon:* (+49) 6201–606-565

**Kurierdienste:**
Boschstraße 12, 69469 Weinheim

**Postanschrift:**
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## Service

## Author Profile

*“My favorite food is Tofu.
If I were not a scientist, I would be a businessman selling green tea. …”*
This and more about Xinchen Wang can be found on page 9610.

## News


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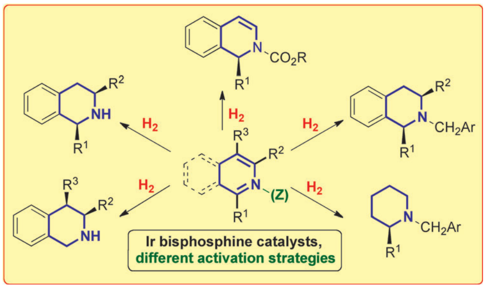
## Books

# Highlights

## Asymmetric Hydrogenation

D. Zhao, F. Glorius* ______ **9616 – 9618**

Enantioselective Hydrogenation of Isoquinolines



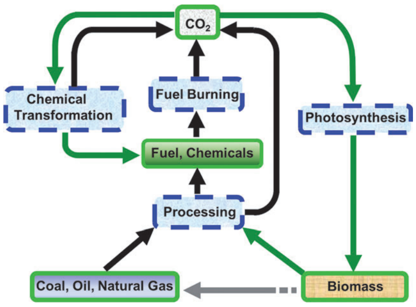
**N-H$_2$eterocycles:** Significant advances have been made in the development of the enantioselective partial or full hydrogenation of substituted isoquinolines and isoquinolinium and pyridinium salts. The products are valuable chiral 1,2,3,4-tetrahydroisoquinolines and piperidines (see scheme).

# Essays

## Sustainable Chemistry

M. He,* Y. Sun,* B. Han* __ **9620 – 9633**

Green Carbon Science: Scientific Basis for Integrating Carbon Resource Processing, Utilization, and Recycling



**How green was my valley**: Green carbon science focuses on the transformations of carbon-containing compounds in the entire carbon cycle. The ultimate aim is to use carbon resources efficiently and minimize the net $CO_2$ emission. This holistic view also has ramifications for related fields including petroleum refining and the production of liquid fuels and chemicals from coal, methane, $CO_2$, and biomass.

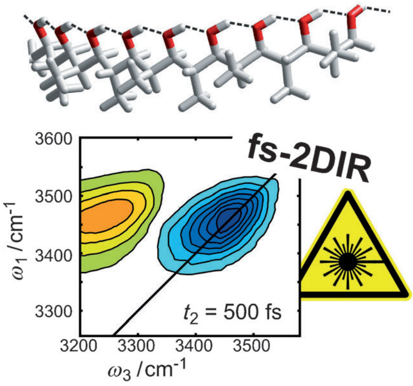
# Reviews

## Femtosecond Spectroscopy

M. Olschewski, S. Knop, J. Lindner, P. Vöhringer* ____________ **9634 – 9654**

From Single Hydrogen Bonds to Extended Hydrogen-Bond Wires: Low-Dimensional Model Systems for Vibrational Spectroscopy of Associated Liquids

**Liquid refreshment**: A random hydrogen-bond network is at the heart of the exceptional physical and chemical properties of liquid water. Femtosecond two-dimensional infrared spectroscopy (2DIR) is a powerful method to obtain structural and dynamical information about hydrogen bonds to isolate the spectroscopic signatures of simultaneous highly diverse molecular dynamic processes in the complex network of associated liquids in real time.



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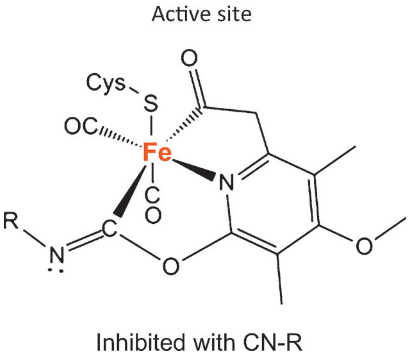
**Inhibition mechanism**: Isocyanides strongly inhibit [Fe]-hydrogenase. X-ray crystallography and X-ray absorption spectroscopy revealed that the isocyanide binds to the *trans* position, versus the acyl carbon of the Fe center, and is covalently bound to the pyridinol hydroxy oxygen. These results also indicated that the hydroxy group is essential for $H_2$ activation.



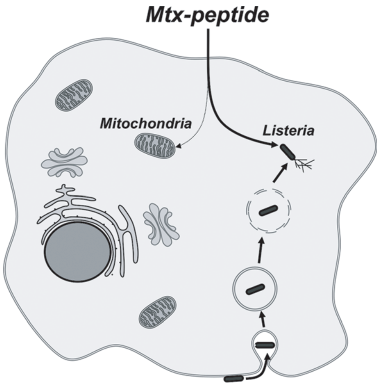
## Bioinorganic Chemistry

H. Tamura, M. Salomone-Stagni, T. Fujishiro, E. Warkentin, W. Meyer-Klaucke, U. Ermler, S. Shima* ——— 9656 – 9659

Crystal Structures of [Fe]-Hydrogenase in Complex with Inhibitory Isocyanides: Implications for the $H_2$-Activation Site

Frontispiece

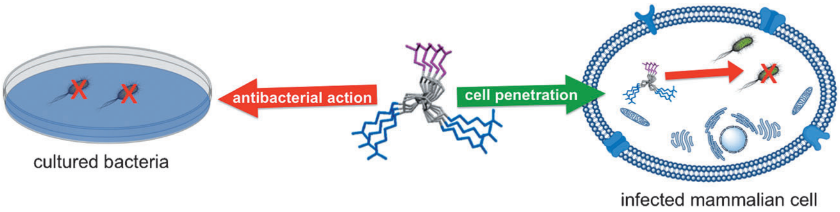
**Engineered vectors for intracellular targeting**: Engineered peptides were used as a methotrexate delivery vector against intracellular *L. monocytogenes*. A peptide library was developed to determine the chemical properties required for specific drug delivery to bacteria while maintaining mitochondrial localization as a drug reservoir. Mtx–peptide conjugates were found to have higher antimicrobial activity and lower human cell toxicity.



## Intracellular Targeting

E. K. Lei, M. P. Pereira, S. O. Kelley* ——— 9660 – 9663

Tuning the Intracellular Bacterial Targeting of Peptidic Vectors



**De novo design** of unnatural proline-rich peptides led to a potent antibacterial peptide that targets both Gram-positive and -negative bacteria. The peptide exerts activity without lysing bacterial membranes or causing hemolysis, and is stable to extended trypsin treatment. Facile entry into macrophages was observed, leading to extensive intracellular clearing of pathogenic bacteria.

## Dual-Action Antibiotic Peptides

J. Kuriakose, V. Hernandez-Gordillo, M. Nepal, A. Brezden, V. Pozzi, M. N. Seleem,* J. Chmielewski* ——— 9664 – 9667

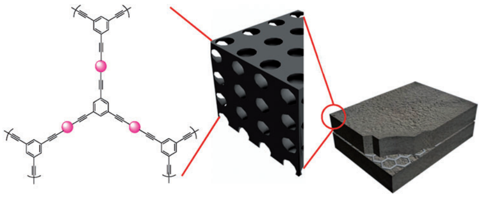
Targeting Intracellular Pathogenic Bacteria with Unnatural Proline-Rich Peptides: Coupling Antibacterial Activity with Macrophage Penetration

## Porous Polymer Sandwiches

X. D. Zhuang, F. Zhang,* D. Wu, N. Forler, H. Liang, M. Wagner, D. Gehrig, M. R. Hansen, F. Laquai, X. Feng* ________ **9668 – 9672**

### Two-Dimensional Sandwich-Type, Graphene-Based Conjugated Microporous Polymers

**Back Cover**



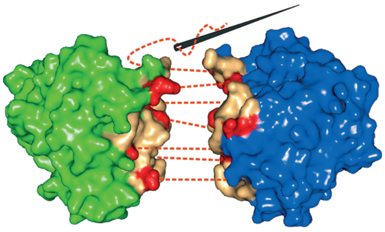
**Better than sliced bread**: Layered two-dimensional graphene-based conjugated microporous polymers, which exhibit high surface areas and fluorescence quenching, can be prepared by a graphene-mediated Sonogashira–Hagihara coupling. Upon thermal pyrolysis, these porous polymers are readily converted into porous carbon materials with intriguing physical and electrochemical properties (see scheme; pink spheres = thiophene, thiazole, or pyridine units).

## Enzyme Catalysis

A. Bosshart, S. Panke, M. Bechtold* ________ **9673 – 9676**

### Systematic Optimization of Interface Interactions Increases the Thermostability of a Multimeric Enzyme

**Stapling subunits**: The limited stability of multimers (see picture) is often associated with subunit dissociation. A novel procedure was applied on the basis of crystal structure analysis, sequence alignment, and single-site saturation mutagenesis to systematically identify residues in the inter-subunit interface suitable for increasing stability.

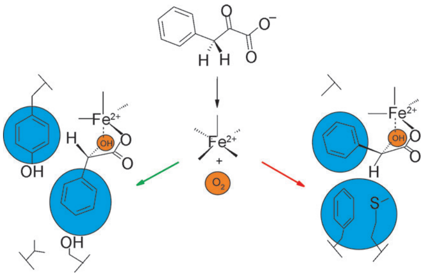


## Biocatalysis

S. M. Pratter, C. Konstantinovics, C. M. L. Di Giuro, E. Leitner, D. Kumar, S. P. de Visser, G. Grogan, G. D. Straganz* ________ **9677 – 9681**

### Inversion of Enantioselectivity of a Mononuclear Non-Heme Iron(II)-dependent Hydroxylase by Tuning the Interplay of Metal-Center Geometry and Protein Structure

**The ol' switcheroo**: The enantioselectivity of an $O_2$-dependent hydroxylation at a mononuclear non-heme iron center was switched from *S* to *R* by changing the geometry of the substrate ligand at the metal center through protein redesign. This rational approach resulted in a greater than 9000-fold enhancement in (*R*)-selectivity and yielded a highly active (*R*)-mandelate synthase.

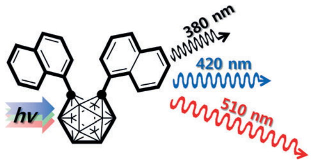


## Photochemistry

K.-R. Wee, Y.-J. Cho, J. K. Song, S. O. Kang* ________ **9682 – 9685**

### Multiple Photoluminescence from 1,2-Dinaphthyl-*ortho*-Carborane

**Naphthyl-substituted *ortho*-carboranes,** which were prepared following the reaction between acetylene and decarborane, showed unique multiple photoluminescence behavior associated with intramolecular charge transfer (see picture). On the basis of theoretical calculations, the photoluminescence is shown to originate from the overlap between the naphthyl π orbital and the carboranyl σ orbital.

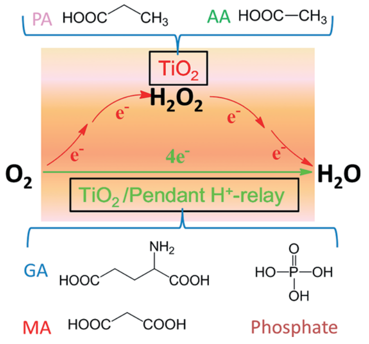


## Photocatalysis

H. Sheng, H. Ji, W. Ma, C. Chen,*
J. Zhao ________ **9686 – 9690**

Direct Four-Electron Reduction of $O_2$ to $H_2O$ on $TiO_2$ Surfaces by Pendant Proton Relay

**Relay race**: By using polyprotic-acid-based pendant proton relays (phosphate, L-glutamic acid, and malonic acid), the oxygen reduction reaction (ORR) on a $TiO_2$ surface is switched from a single-electron process to a concerted 4 $e^-$/4 $H^+$ reduction to $H_2O$. In contrast, monocarboxylic acids (PA and AA) without pendant proton relays only enhance the ORR reduction rate but barely change the reaction pathway.

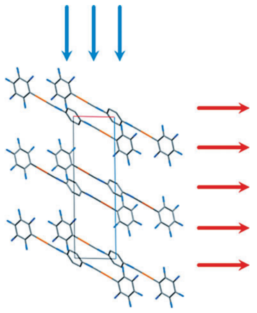


## High-Pressure Crystallography

C. H. Woodall, C. M. Beavers,
J. Christensen, L. E. Hatcher, M. Intissar,
A. Parlett, S. J. Teat, C. Reber,*
P. R. Raithby* ________ **9691 – 9694**

Hingeless Negative Linear Compression in the Mechanochromic Gold Complex $[(C_6F_5Au)_2(\mu\text{-}1,4\text{-diisocyanobenzene})]$

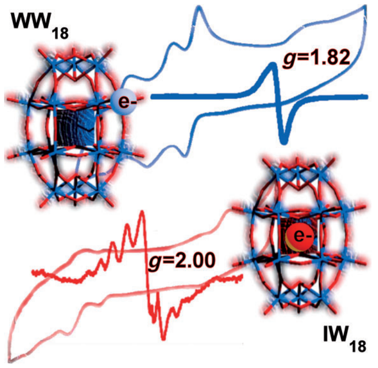
**Growing under pressure**: High-pressure crystallographic and Raman spectroscopic studies show that crystals of the linear digold complex $[(C_6F_5Au)_2(\mu\text{-}1,4\text{-diisocyanobenzene})]$ undergo substantial negative linear compression over the pressure range from ambient to 4.39 GPa.



## Inner-Cluster Radicals

L. Vilà-Nadal, K. Peuntinger, C. Busche,
J. Yan, D. Lüders, D.-L. Long,
J. M. Poblet,* D. M. Guldi,*
L. Cronin* ________ **9695 – 9699**

Polyoxometalate $\{W_{18}O_{56}XO_6\}$ Clusters with Embedded Redox-Active Main-Group Templates as Localized Inner-Cluster Radicals



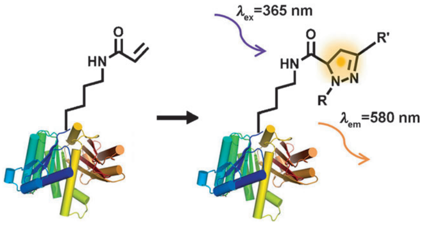
**Non-mixed-valent** reduced polyoxometalates, namely $\{W_{18}O_{56}XO_6\}$ Dawson-like clusters ($X = I^{VII}$ or $Te^{VI}$) with a localized redox active template have been synthesized and redox properties compared with the pure tungsten control (that is, $X = W^{VI}$). Upon one-electron reduction, the electron localizes on the main-group element, giving $I^{VI}$ or $Te^{V}$, respectively. These clusters have potential as a new type of electron-transfer reagent.

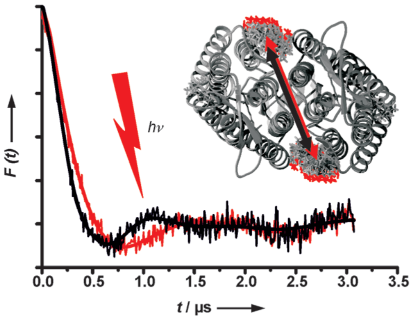
## Synthetic Biology

F. H. Li, H. Zhang, Y. Sun, Y. C. Pan,
J. Z. Zhou, J. Y. Wang* ____ **9700 – 9704**

Expanding the Genetic Code for Photoclick Chemistry in *E. coli*, Mammalian Cells, and *A. thaliana*

**Breaking the (genetic) code**: *N*-ε-acryllysine was genetically incorporated into proteins in bacterial cells, mammalian cells, and *Arabidopsis thaliana* by co-expressing a pyrrolysyl-tRNA mutant synthetase and its cognate tRNA in the model organism. A photoclick reaction driven by irradiation by 365 nm UV light or 405 nm laser light and allowed for site-specific protein labeling within minutes both in vitro and in vivo.





**A protein photoswitch**: Site-directed spin labeling was applied to monitor conformational changes of channelrhodopsin-2. Double electron electron resonance spectroscopy reveals interspin distance changes upon light activation which can be attributed to a displacement of the cytoplasmic part of the transmembrane helix B (see picture). This helix movement could be part of the channel opening mechanism.

### Membrane Proteins

T. Sattig, C. Rickert, E. Bamberg,
H.-J. Steinhoff,*
C. Bamann* ______ **9705 – 9708**

Light-Induced Movement of the Transmembrane Helix B in Channelrhodopsin-2

**Inside Cover**

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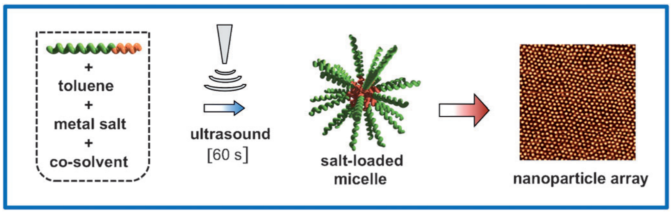

**A rapid and facile route** allows the self-assembly of precursor micelles loaded with metal salts on an unprecedented short timescale. Micellar arrays can then be transformed into high-quality (metal or metal oxide) nanoparticle arrays. This promising route offers functionalization of surfaces by nanomaterials on industrially relevant timescales.

### Ordered Nanostructures

A. Ethirajan,* S. Punniyakoti,
M. D'Olieslaeger, P. Wagner
H.-G. Boyen ______ **9709 – 9713**

Ultrafast Self-Assembly Using Ultrasound: A Facile Route to the Rapid Fabrication of Well-Ordered Dense Arrays of Inorganic Nanostructures

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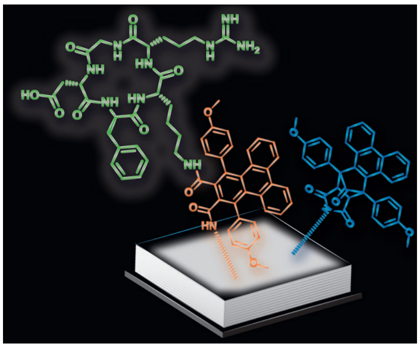


**A phencyclone** derivative is used to achieve light-controlled immobilization of peptides possessing only natural amino acids. The photoactive precursor (blue in picture) is formed in a Diels–Alder reaction and can undergo light-triggered ring-opening reactions with amines. Successful surface patterning with a genuine c-(RGDfK) peptide (green) is evidenced by imaging time-of-flight secondary-ion mass spectrometry (ToF-SIMS).

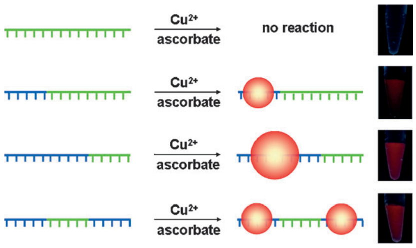
### Photopatterning

T. Pauloehrl, A. Welle, M. Bruns, K. Linkert,
H. G. Börner, M. Bastmeyer, G. Delaittre,
C. Barner-Kowollik* ______ **9714 – 9718**

Spatially Controlled Surface Immobilization of Nonmodified Peptides

---

**Fitting (nanoparticles) to a T**: Single-stranded DNA poly T (blue, see scheme) was found to be a template for the formation of fluorescent copper nanoparticles (CuNPs, red spheres). The size and fluorescence of these CuNPs could be regulated by altering the length of poly T. Other ssDNAs (green) failed to act as a template for CuNPs and were used to create alternating metallized and non-metallized nanostructures.



### Nanoparticle Synthesis

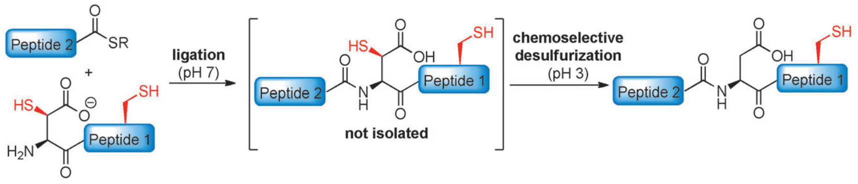
Z. Qing, X. He, D. He, K. Wang,* F. Xu,
T. Qing, X. Yang ______ **9719 – 9722**

Poly(thymine)-Templated Selective Formation of Fluorescent Copper Nanoparticles

## Peptide Ligation

R. E. Thompson, B. Chan, L. Radom,
K. A. Jolliffe, R. J. Payne* ___ **9723 – 9727**

Chemoselective Peptide Ligation–Desulfurization at Aspartate



**Asp-ecially useful**: A synthetic β-mercapto aspartate residue facilitates the rapid ligation to a range of peptide thioesters. Following the ligation reaction (and without purification), chemoselective desulfurization of the β-mercapto moiety in the presence of unprotected cysteine residues afforded native peptide products.

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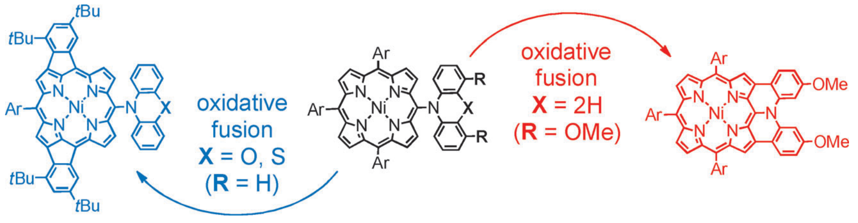
## Porphyrinoids

N. Fukui, W.-Y. Cha, S. Lee, S. Tokuji,
D. Kim,* H. Yorimitsu,*
A. Osuka* ___ **9728 – 9732**

Oxidative Fusion Reactions of meso-(Diarylamino)porphyrins



**Creating cool fusion**: The oxidative fusion of meso-(diarylamino)porphyrins depends heavily on the structures of the diarylamino groups. Bridged diarylamino groups result in the oxidative fusion of 3,5-di-*tert*-butylphenyl groups to the porphyrin moiety (blue), while non-bridged diarylamino groups invoke formation of nitrogen-embedded aminophenylene-fused porphyrins (red).

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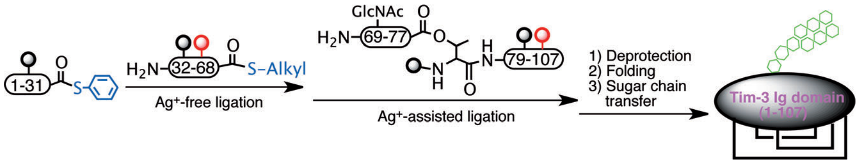
## Glycoprotein Synthesis

Y. Asahina, S. Kamitori, T. Takao, N. Nishi,
H. Hojo* ___ **9733 – 9737**

Chemoenzymatic Synthesis of the Immunoglobulin Domain of Tim-3 Carrying a Complex-Type N-Glycan by Using a One-pot Ligation



**Ligations**: The title immunoglobin (Ig) domain was chemoenzymatically synthesized. The domain was divided into three segments and N- and S-protected peptide thioesters were synthesized by solid-phase peptide synthesis. The one-pot sequential ligation was achieved by using $Ag^+$-free and $Ag^+$-assisted activation of the thioester. After folding and enzymatic transfer of the synthetic glycan, the desired Ig domain carrying a nonasaccharide was successfully obtained.

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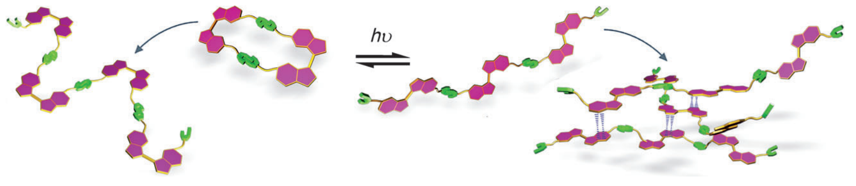
## Supramolecular Polymers

J.-F. Xu, Y.-Z. Chen, D. Wu, L.-Z. Wu,
C.-H. Tung, Q.-Z. Yang* ___ **9738 – 9742**

Photoresponsive Hydrogen-Bonded Supramolecular Polymers Based on a Stiff Stilbene Unit

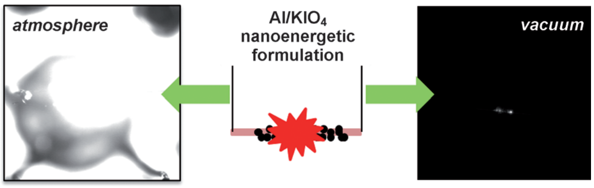


**The state of play**: The polymerization mechanism and properties of photoresponsive hydrogen-bonded supramolecular polymers formed from a stiff stilbene with two ureidopyrimidinone moieties depend strongly on the isomeric state of the chromophore. Electrospinning the polymer formed from the *Z* isomer yield fluorescent nanofibers, while the *E* analogue forms a multiresponsive gel.

## Energetic Materials

G. Q. Jian, J. Y. Feng, R. J. Jacob,
G. C. Egan,
M. R. Zachariah* ________ **9743 – 9746**

### Super-reactive Nanoenergetic Gas Generators Based on Periodate Salts



**Nanoenergetic formulations under flash heating**: Periodate salt nanoparticles are synthesized by a facile aerosol spray drying process and demonstrate highly reactive properties as oxidizers in an aluminum-based nanoenergetic formulation. Direct evidence supports that gas phase oxygen release from the oxidizer decomposition is critical in the ignition and combustion of these formulations.

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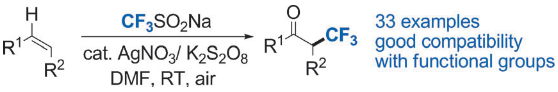
## Trifluoromethylation

A. Deb, S. Manna, A. Modak, T. Patra,
S. Maity, D. Maiti* ________ **9747 – 9750**

### Oxidative Trifluoromethylation of Unactivated Olefins: An Efficient and Practical Synthesis of α-Trifluoromethyl-Substituted Ketones



**An economical approach** to α-CF$_3$-substituted ketones, which are important intermediates in synthetic and medicinal chemistry, employs olefins and the readily available Langlois reagent (CF$_3$SO$_2$Na). The reaction is operationally simple, proceeds at room temperature, and exhibits an excellent tolerance toward a wide variety of functional groups.

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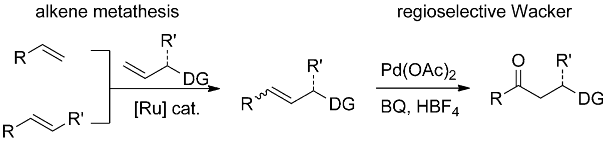
## Synthetic Methods

B. Morandi, Z. K. Wickens,
R. H. Grubbs* ________ **9751 – 9754**

### Regioselective Wacker Oxidation of Internal Alkenes: Rapid Access to Functionalized Ketones Facilitated by Cross-Metathesis



**Wacka wacka**: The title reaction makes use of a wide range of directing groups (DG) to enable the highly regioselective oxidation of alkenes, and occurs predictably at the distal position. Both *E* and *Z* alkenes afford valuable functionalized ketones and cross-metathesis was shown to facilitate the preparation of the starting materials. BQ = benzoquinone.

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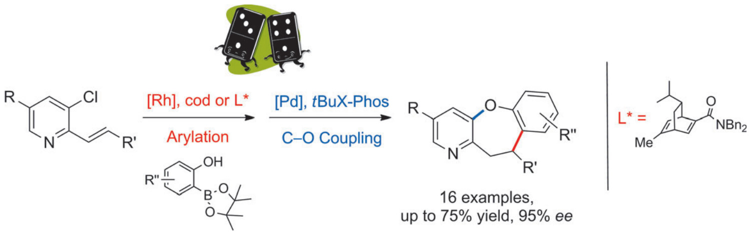
## Multi-Catalytic Reactions

A. A. Friedman, J. Panteleev, J. Tsoung,
V. Huynh, M. Lautens* ________ **9755 – 9758**

### Rh/Pd Catalysis with Chiral and Achiral Ligands: Domino Synthesis of Aza-Dihydrodibenzoxepines



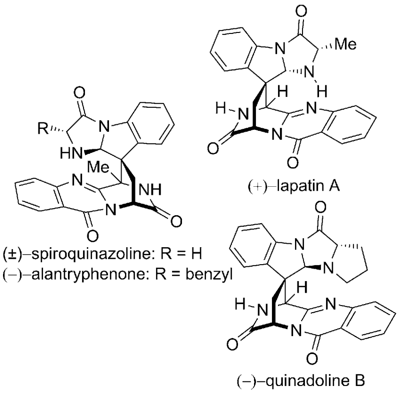
**A game of dominoes**: A synthetic route to aza-dihydrodibenzoxepines is described, through the combination of a Rh-catalyzed arylation and a Pd-catalyzed C-O coupling in a single pot. For the first time, the ability to incorporate a chiral and an achiral ligand in a two-component, two-metal transformation is achieved, giving the products in moderate to good yields, with excellent enantioselectivities.

## Natural Products Synthesis

M. Wu, D. Ma* ____________ **9759 – 9762**

Total Syntheses of (±)-Spiroquinazoline, (−)-Alantryphenone, (+)-Lapatin A, and (−)-Quinadoline B

**Quick access**: The aza-Diels–Alder reaction of unprecedented aminal-embodied olefins with azadienes provides quick access to indoline-containing spiroquinazoline alkaloids. This approach was utilized in the total syntheses of the title compounds (see figure).



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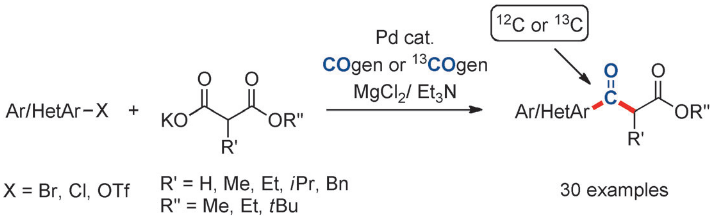
## Palladium Catalysis

S. Korsager, D. U. Nielsen, R. H. Taaning,* T. Skrydstrup* ____________ **9763 – 9766**

Access to β-Keto Esters by Palladium-Catalyzed Carbonylative Coupling of Aryl Halides with Monoester Potassium Malonates



**New tricks for an old dog**: The Pd-catalyzed carbonylative α-arylation of monoethyl potassium malonates with aryl bromides and reactive aryl chlorides provides a simple and direct route to aryl β-ketoesters. Because only stoichiometric amounts of carbon monoxide are employed, the method is ideal for the introduction of carbon isotopes into more complex structures.

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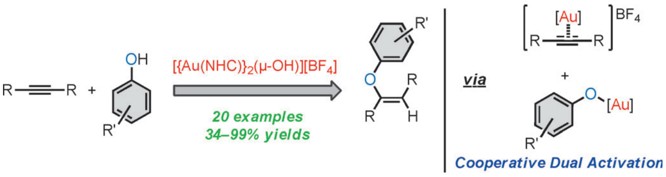
## Cooperative Catalysis

Y. Oonishi, A. Gómez-Suárez, A. R. Martin, S. P. Nolan* __ **9767 – 9771**

Hydrophenoxylation of Alkynes by Cooperative Gold Catalysis



**Double impact**: The title method gives aryl vinyl ethers in high yields, short reaction times, *Z*-stereospecificity, and good regioselectivities. Insights into the reaction mechanism highlight the role of $[\{Au(NHC)\}_2(\mu\text{-}OH)][BF_4]$ (NHC = N-heterocyclic carbene) as both a Lewis acid, $[Au(NHC)][BF_4]$, and a Brønsted base, $[Au(NHC)(OH)]$, thereby generating a synergistic effect between the two gold moieties.

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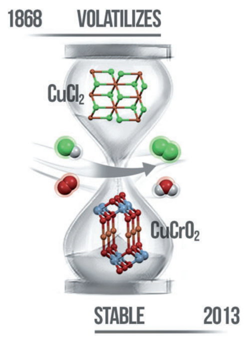
## Heterogeneous Catalysis

A. P. Amrute, G. O. Larrazábal, C. Mondelli, J. Pérez-Ramírez* ____________ **9772 – 9775**

$CuCrO_2$ Delafossite: A Stable Copper Catalyst for Chlorine Production

**Front Cover**

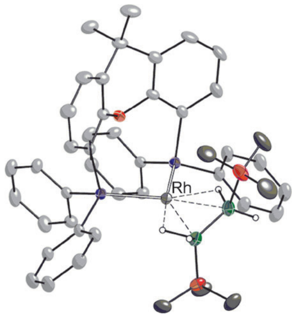


**With time comes wisdom**: Since the implementation of $CuCl_2$ for HCl oxidation by Deacon in 1868, the search for stable copper catalysts has been futile. Cuprous delafossite, $CuCrO_2$ (see picture), is shown to have unprecedented stability against chlorination, allowing for durable $Cl_2$ production with no metal loss. Based on this, a highly active $CuCrO_2$-$CeO_2$ composite was developed, a cost-effective $Cl_2$ recovery method.

## B-B Coupling

H. C. Johnson, C. L. McMullin, S. D. Pike,
S. A. Macgregor,*
A. S. Weller* ____________ **9776 – 9780**

Dehydrogenative Boron Homocoupling of an Amine-Borane



**A meeting of borons**: The homocoupling of a B–B bond in an amine-borane is reported to give a diborane coordinated to a $Rh^{I}$ metal center (see picture; C gray/black, O red, P blue, B green, N orange). The pathway for the occurrence of this reaction was also studied using density functional theory to calculate the free energies of each intermediate.

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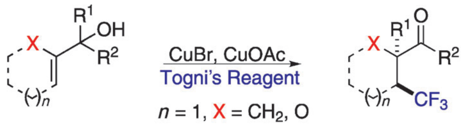
## Trifluoromethylation

Z.-M. Chen, W. Bai, S.-H. Wang,
B.-M. Yang, Y.-Q. Tu,*
F.-M. Zhang ____________ **9781 – 9785**

Copper-Catalyzed Tandem Trifluoromethylation/Semipinacol Rearrangement of Allylic Alcohols



**Tandem jump**: A novel copper-catalyzed tandem trifluoromethylation/semipinacol rearrangement reaction of allylic alcohols has been achieved under mild conditions. This reaction is valuable for the difunctionalization of alkenes through simultaneous construction of a $C_{sp^3}$–$CF_3$ bond and a quaternary carbon center, and could provide a straightforward strategy for the preparation of α-quaternary β-trifluoromethyl ketone derivatives.

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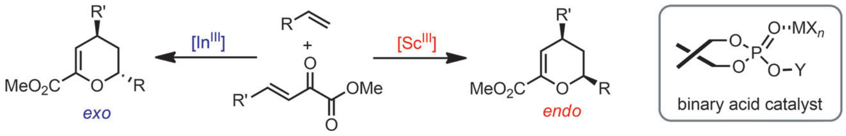
## Asymmetric Catalysis

J. Lv, L. Zhang, S. Luo,*
J.-P. Cheng ____________ **9786 – 9790**

Switchable Diastereoselectivity in Enantioselective [4+2] Cycloadditions with Simple Olefins by Asymmetric Binary Acid Catalysis



**The exchange** of the metal ion from $In^{III}$ to $Sc^{III}$ in a binary acid catalyst leads to a switch in the diastereoselectivity of [4+2] cycloadditions. Simple olefins and β,γ-unsaturated α-ketoester were thus transformed to the corresponding *exo* or *endo* products, respectively, with excellent diastereoselectivity (up to 99:1 d.r.) and enantioselectivity (up to 99% *ee*).

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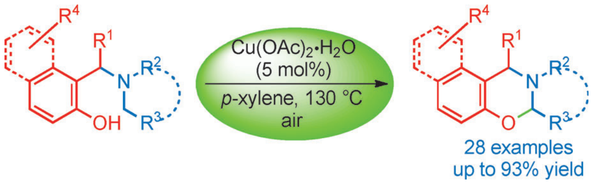
## C–H Activation

M. L. Deb, S. S. Dey, I. Bento,
M. T. Barros,
C. D. Maycock* ____________ **9791 – 9795**

Copper-Catalyzed Regioselective Intramolecular Oxidative α-Functionalization of Tertiary Amines: An Efficient Synthesis of Dihydro-1,3-Oxazines

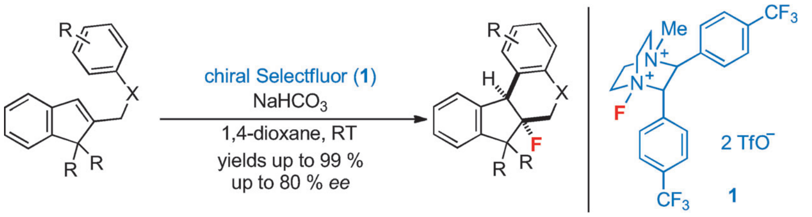


**Traffic control**: The hydroxy functional group directs the α-functionalization of tertiary amines, synthesizing 1,3-oxazines by C–O bond formation. Reaction occurs with both benzylic and non-benzylic amines. In the case of naphthoxazine synthesis, 100% diastereoselectivity was observed. A tentative two-pathway mechanism is proposed for the reaction.

## Synthetic Methods

J. R. Wolstenhulme, J. Rosenqvist,
O. Lozano, J. Ilupeju, N. Wurz,
K. M. Engle, G. W. Pidgeon, P. R. Moore,
G. Sandford,
V. Gouverneur* ______ **9796 – 9800**

Asymmetric Electrophilic Fluorocyclization with Carbon Nucleophiles

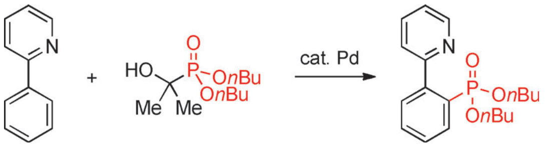


**Twist of 'F'ate**: Various helical-shaped fluorinated tetracyclic molecules were prepared by fluorocarbocyclization of prochiral alkenes. The development of a new class of chiral Selectfluor (**1**) proved instrumental in developing an asymmetric variant of this transformation. These novel chiral N-F reagents are readily accessible by fluorine transfer from shelf-stable *N*-fluoropyridinium salts.

## C–H Phosphonation

C. Li, T. Yano, N. Ishida,
M. Murakami* ______ **9801 – 9804**

Pyridine-Directed Palladium-Catalyzed Phosphonation of C(sp$^2$)–H Bonds

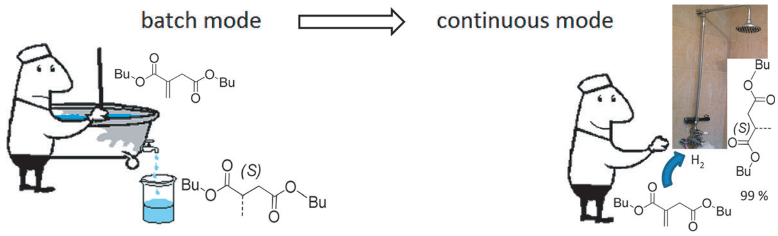


**Follow the guide**: The palladium-catalyzed phosphonation of a C(sp$^2$)–H bond occurs through the use of a pyridyl group as the directing group. α-Hydroxyalkylphosphonate is used as the phosphonating reagent (see scheme).

## Solventless Synthesis

R. Duque, P. J. Pogorzelec,
D. J. Cole-Hamilton* ______ **9805 – 9807**

A Single Enantiomer (99%) Directly from Continuous-Flow Asymmetric Hydrogenation

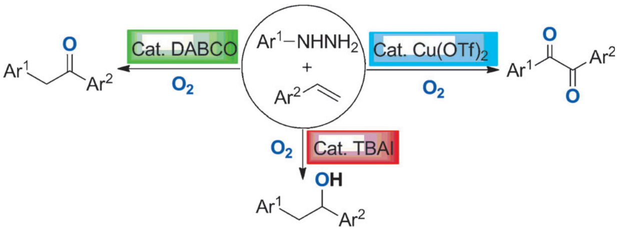


**Chemistry in a shower**: Dibutyl itaconate is hydrogenated in a solventless reaction to dibutyl (*S*)-(–)-methylsuccinate at ambient temperature and 5 bar. The product is recovered directly from a flow system.

## Dioxygen Activation

Y. Su, X. Sun, G. Wu,
N. Jiao* ______ **9808 – 9812**

Catalyst-Controlled Highly Selective Coupling and Oxygenation of Olefins: A Direct Approach to Alcohols, Ketones, and Diketones

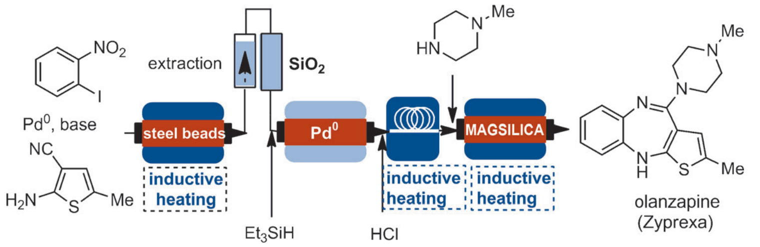


**Oxygen? That's radical!** A method for the direct synthesis of substituted alcohols, ketones, and diketones through a catalyst-controlled highly chemoselective coupling and oxygenation of olefins has been developed. The method is simple and practical, can be switched by the selection of different catalysts, and employs molecular oxygen as both an oxidant and a reagent.

## *Flow Synthesis*

J. Hartwig, S. Ceylan, L. Kupracz, L. Coutable, A. Kirschning* **9813 – 9817**

Heating under High-Frequency Inductive Conditions: Application to the Continuous Synthesis of the Neurolepticum Olanzapine (Zyprexa)



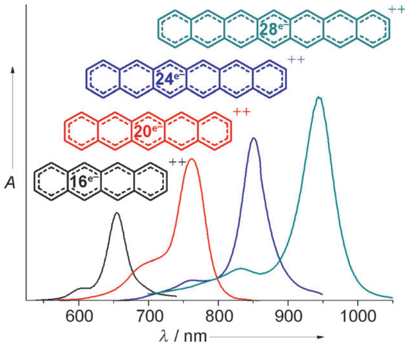
**Hot chemistry!** High-frequency inductive heating and flow chemistry are an ideal match for high-temperature synthesis. This is demonstrated in the multistep flow synthesis of the neurolepticum olanzapine (Zyprexa) that included three reactions with inductive heating and two purification steps conducted as continuous processes.

---

## *Acene Dications*

R. Einholz, H. F. Bettinger* **9818 – 9820**

Heptacene: Increased Persistence of a $4n+2$ π-Electron Polycyclic Aromatic Hydrocarbon by Oxidation to the $4n$ π-Electron Dication



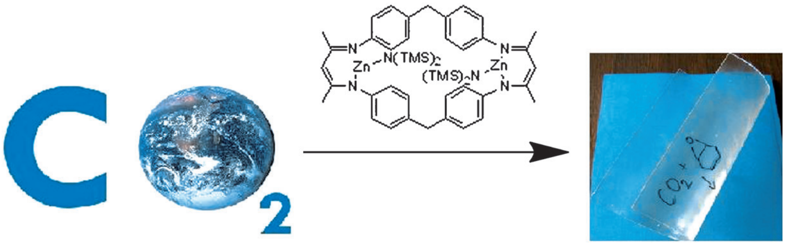
**An unexpectedly stable dication**: Heptacene (a $4n+2$ π-electron compound) is so highly reactive that it cannot be isolated. Its dication (a $4n$ π-electron compound) can be obtained from heptacene dimers/oligomers in sulfuric acid at room temperature and can be kept for more than one year in the absence of oxygen. (See picture for the UV/Vis-NIR spectra of the dications of tetracene to heptacene.)

---

## *Copolymerization*

M. W. Lehenmeier, S. Kissling, P. T. Altenbuchner, C. Bruckmeier, P. Deglmann, A.-K. Brym, B. Rieger* **9821 – 9826**

Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in $CO_2$/Epoxide Copolymerization Catalysis?

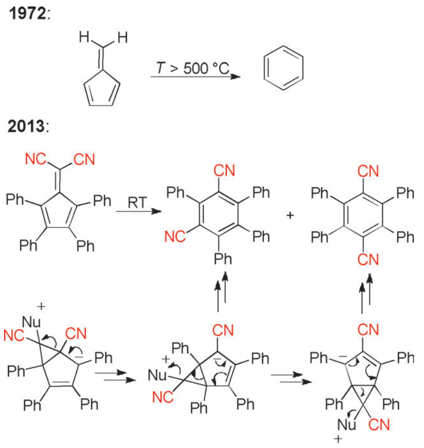


**Working in zinc**: Kinetic investigations of a new zinc catalyst (see scheme) for the copolymerization of $CO_2$ and epoxides show a reversible shift in the rate-determining step from epoxide ring opening to $CO_2$ insertion, depending on the applied pressure. This shift is attributed to the similarity of the activation barriers and explains the exceptionally high activities for the copolymerization.

## Fulvenes

A. D. Finke, S. Haberland,
W. B. Schweizer, P. Chen,
F. Diederich* ____________ **9827 – 9830**

A Mild, Thermal Pentafulvene-to-Benzene Rearrangement

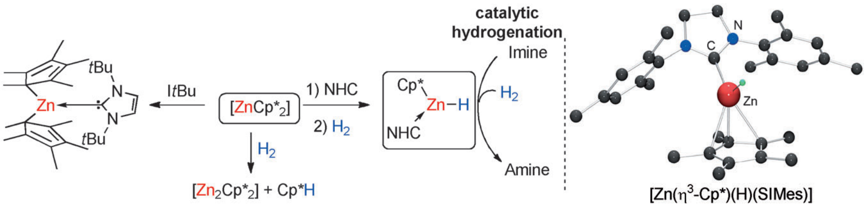


**Walk this way**: More than 40 years after the discovery that fulvene can thermally rearrange to benzene at high temperatures, it has been found that 6,6-dicyanopentafulvenes can rearrange quantitatively to 1,3- and 1,4-dicyanobenzenes under mild conditions in polar aprotic solvents. A polar "ring-walk" mechanism is proposed to explain this unprecedented reactivity.

## Zinc-Catalyzed Hydrogenation

P. Jochmann,
D. W. Stephan* ____________ **9831 – 9835**

$H_2$ Cleavage, Hydride Formation, and Catalytic Hydrogenation of Imines with Zinc Complexes of $C_5Me_5$ and N-Heterocyclic Carbenes



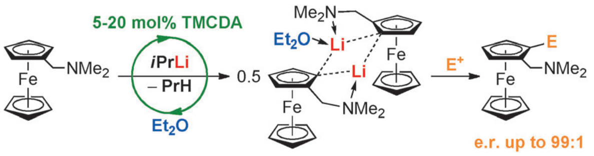
**Decamethylzincocene**, $[ZnCp^*_2]$, reacts with $H_2$ to give the reduced $Zn^I$ compound $[Zn_2Cp^*_2]$. In the presence of coordinating and (more efficiently) of non-coordinating N-heterocyclic carbenes (NHCs), the catalytic hydrogenation of imines with $H_2$ is achieved. The monomeric hydride [Zn(Cp*)(H)(SIMes)] is presented and its mechanistic implications are considered.

## Chiral Metallocenes

P. Steffen, C. Unkelbach, M. Christmann,
W. Hiller, C. Strohmann* ____ **9836 – 9840**

Catalytic and Stereoselective *ortho*-Lithiation of a Ferrocene Derivative

**Inside Back Cover**

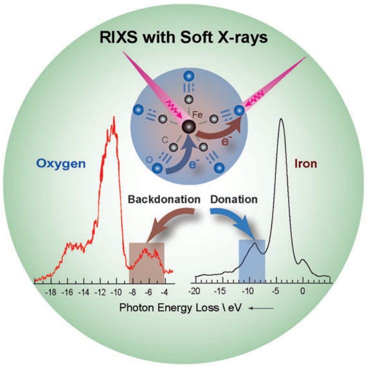


***N*****,*****N*****-Dimethylferrocenylmethylamine** can be lithiated stereoselectively by *i*PrLi in pentane/$Et_2O$ using catalytic amounts of the chiral auxiliary (*R*,*R*)-TMCDA. In homogenous reactions, high e.r. values were obtained upon crystallization of the lithiated species. The catalytic activity of TMCDA is made possible by its release from the stereomerically pure lithioferrocene as it dimerizes to a homochiral dimeric etherate.

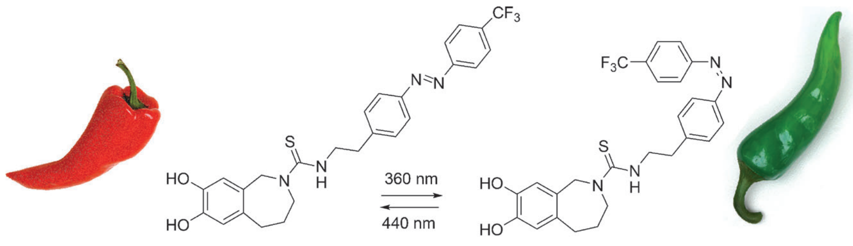
## Molecular Orbital Mixing

E. Suljoti, R. Garcia-Diez, S. I. Bokarev,*
K. M. Lange, R. Schoch , B. Dierker,
M. Dantz, K. Yamamoto, N. Engel, K. Atak,
O. Kühn, M. Bauer,* J.-E. Rubensson,
E. F. Aziz* ____________ **9841 – 9844**

Direct Observation of Molecular Orbital Mixing in a Solvated Organometallic Complex



**Fundamental processes**: Charge donation/backdonation in the $[Fe(CO)_5]$ molecule in solution was measured by resonant inelastic X-ray scattering. This method can be used to selectively probe the electronic structure at each atom in the iron–carbonyl bond.



**Controlling pain with light**: TRPV1 channels mediate the response to noxious heat and can be activated by capsaicin, the major ingredient of chili pepper. Novel azobenzene photoswitches can be used for the optical control of TRPV1. One of these compounds antagonizes capsaicin in a light-dependent fashion, demonstrating that a photoswitchable antagonist and an agonist can be applied in concert to modulate ion channel activity.

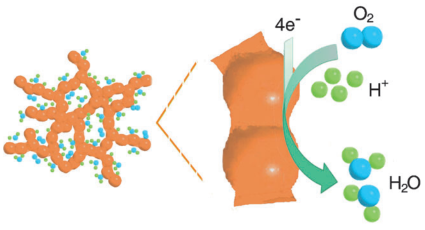
## Photopharmacology

M. Stein, A. Breit, T. Fehrentz,
T. Gudermann, D. Trauner* . **9845 – 9848**

Optical Control of TRPV1 Channels

---

**Best of both worlds**: $Pt_xPd_y$, Pt, and Pd aerogels with high surface area and porosity can be synthesized in a controlled fashion by a straightforward and environmentally benign strategy. These materials, which are highly active and stable catalysts for the oxygen reduction reaction in PEFC cathodes, combine the high stability of extended surfaces with the high surface area of nanoparticles.



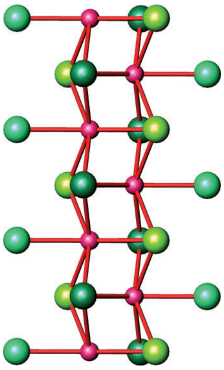
## Electrode Materials

W. Liu, P. Rodriguez, L. Borchardt,
A. Foelske, J. Yuan, A.-K. Herrmann,
D. Geiger, Z. Zheng, S. Kaskel,
N. Gaponik, R. Kötz, T. J. Schmidt,*
A. Eychmüller* ________ **9849 – 9852**

Bimetallic Aerogels: High-Performance Electrocatalysts for the Oxygen Reduction Reaction

---

**The first binary phase** in the system Co-Bi was obtained by high-pressure high-temperature synthesis. The $NiBi_3$-type structure motif comprises cobalt-centered monocapped bismuth prisms with covalent Co-Bi interactions. The polyhedra are condensed into infinite columns (see picture), which are arranged in the form of a distorted hexagonal rod packing. The new compound is a superconductor with a $T_c$ slightly below 0.5 K.



## Binary Supraconductors

U. Schwarz,* S. Tencé, O. Janson, C. Koz,
C. Krellner, U. Burkhardt, H. Rosner,
F. Steglich, Yu. Grin ______ **9853 – 9857**

$CoBi_3$: A Binary Cobalt–Bismuth Compound and Superconductor

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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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