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:

*F. P. C. Binder, K. Lemme, R. C. Preston, B. Ernst**
Sialyl Lewis^x: A "Pre-organized Water Oligomer"?

F. Meemken, N. Maeda, K. Hungerbühler, A. Baiker**
Platinum-Catalyzed Asymmetric Hydrogenation: Spectroscopic Evidence for a O-H-O Hydrogen-Bond Interaction between Substrate and Modifier

*L. Harmand, S. Cadet, B. Kauffmann, L. Scarpantonio, P. Batat, G. Jonusauskas, N. D. McClenaghan, D. Lastécouères, J. Vincent**
Copper Catalyst Activation Driven by Photoinduced Electron Transfer: A Prototype Photolatent Click Catalyst

Author Profile

"If I were not a scientist, I would be an archaeologist. My biggest motivation is my own interest and curiosity …"
This and more about Jinbo Hu can be found on page 6818.

News

V. K. Aggarwal

S. Balasubramanian

D. Klenerman

S. G. Withers

Books

Fragments of Fullerenes and Carbon Nanotubes

Marina A. Petrukhina, Lawrence T. Scott

Highlights

Electrostatic Charging

The Unpredictability of Electrostatic Charging

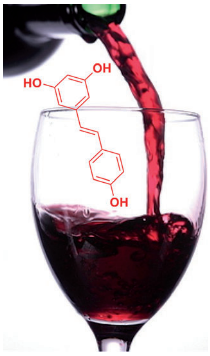
Capricious charges: The electrostatic charging that occurs when two surfaces come into contact is familiar to everyone, and has been known for millennia. Nonetheless, the scientific understanding of the phenomenon is poor, and it is not possible to reliably predict which surface will charge positively and which will charge negatively. Recent work shows why electrostatic charging may never be predictable.

Plant Polyphenols

S. Quideau,* D. Deffieux,
L. Pouységu ______ **6824 – 6826**

Resveratrol Still Has Something To Say about Aging!

A votre Santé! The mechanism by which resveratrol, a hydroxystilbenoid polyphenol found in grapes and present in wine, exerts antiaging metabolic benefits has been uncovered. Chung and co-workers have found that it works by inhibiting cAMP phosphodiesterases, thus triggering a signaling cascade that leads to the possible activation of the mammalian enzyme sirtuin 1.



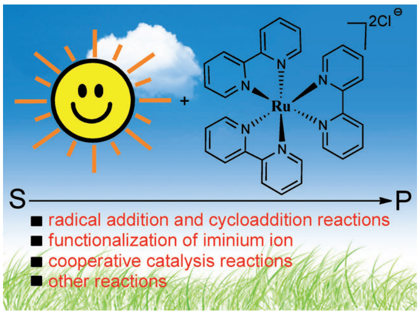
Minireviews

Photoredox Catalysis

J. Xuan, W.-J. Xiao* ______ **6828 – 6838**

Visible-Light Photoredox Catalysis

In the spotlight: The title catalysis is an area of research that is developing quickly and has become a powerful and efficient tool in synthetic organic chemistry (see picture, S = Substrates, P = Products). There is little doubt that continued exploration of visible light photoredox catalysis will uncover a wide range of fascinating and useful chemical reactions.

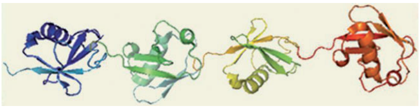


Reviews

Ubiquitin Conjugates

L. Spasser, A. Brik* ______ **6840 – 6862**

Chemistry and Biology of the Ubiquitin Signal



Despite enormous effort, important questions concerning ubiquitination remain unanswered. A major hurdle is the difficulty in obtaining homogeneous ubiquitin bioconjugates. Recent breakthroughs in chemical and semisynthetic strategies now offer a solution to this problem, by enabling the production of larger amounts of such conjugates.

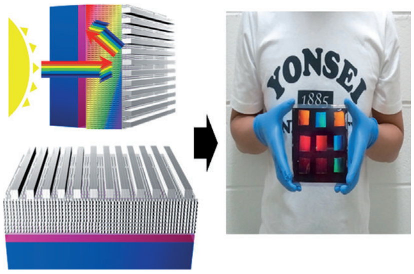
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. 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.

Light Harvesting

J. Kim, J. K. Koh, B. Kim, J. H. Kim,*
E. Kim* ________________ **6864 – 6869**

Nanopatterning of Mesoporous Inorganic Oxide Films for Efficient Light Harvesting of Dye-Sensitized Solar Cells

Frontispiece



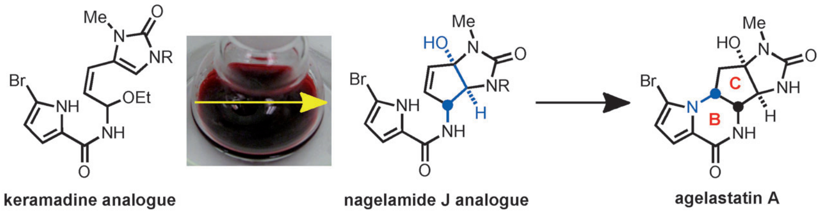
Nanopatterning provides facile process to well-arrayed mesoporous inorganic oxide films at low cost by using readily available pastes and elastomeric nanostamps. The fabricated nanopattern boosted the light-harvesting efficiency of dye-sensitized solar cells (DSSCs) by a light-trapping technique. The iodine-free solid-state DSSCs showed a 40% increase in the current density and high efficiency (7.03%).

Natural Product Synthesis

J. C. P. Reyes, D. Romo* ____ **6870 – 6873**

Bioinspired Total Synthesis of Agelastatin A

Back Cover

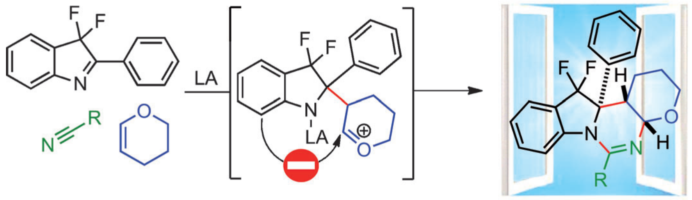


A one-two punch: Two potentially biosynthetically relevant cyclizations of a keramadine analogue give agelastatin A (see scheme). A diastereoselective C-ring formation, which proceeds through a 5-*exo*-trig cyclization or a Nazarov cyclization of a red-colored *N*-acyliminium intermediate, generates the three contiguous stereocenters of the cyclopentane core. A silica gel assisted cyclization of a nagelamide J analogue gives agelastatin A.

Multicomponent Reactions

S. Preciado, E. Vicente-García, S. Llabrés,
F. J. Luque, R. Lavilla* _____ **6874 – 6877**

Exploration of Forbidden Povarov Processes as a Source of Unexpected Reactivity: A Multicomponent Mannich–Ritter Transformation



When a door closes, a window opens! The use of geometrically or electronically restricted imines for Povarov-type processes does not afford the anti-Bredt tetrahydroquinolines, but leads instead to highly functionalized structures through novel reaction pathways (see picture; LA = Lewis acid). The exploration of "forbidden" routes constitutes a valuable approach in the search for new multicomponent reactions.

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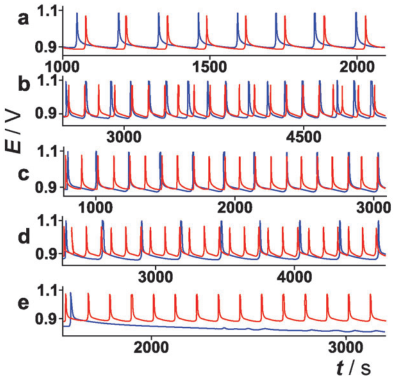


Finger on the pulse: In a system of two pulse-coupled Belousov–Zhabotinsky oscillators, introducing a time delay or increasing the coupling strength brings about novel dynamic features (see picture, the two oscillators are shown in different colors), such as reversal of the roles of excitatory and inhibitory coupling or fast anti-phase oscillation. These features are not observed in diffusively coupled systems, and shed light on how such pulse coupling occurs at synapses.

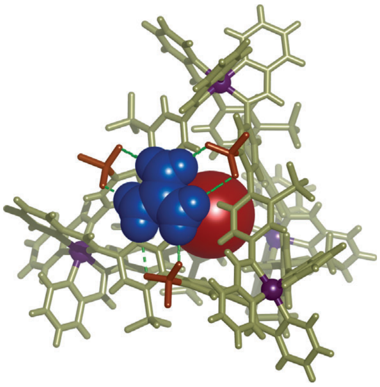
Coupled Oscillators

VIP

V. Horvath, P. L. Gentili, V. K. Vanag,
I. R. Epstein* ____________ **6878 – 6881**

Pulse-Coupled Chemical Oscillators with Time Delay

Take it slow! A metal–organic container molecule has been shown to bind guanidinium cations (blue) between the sulfonate groups on its periphery, as well as accommodating guests such as cyclopentane and cyclohexane in its internal cavity (red). Kinetic studies on the system demonstrated a linear relationship between the amount of bound guanidinium ions and the rate of guest exchange.



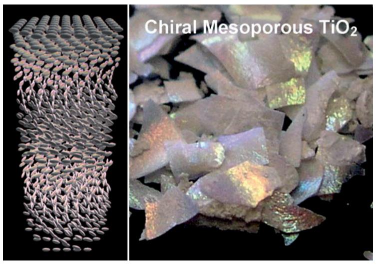
Molecular Capsules

S. Zarra, M. M. J. Smulders, Q. Lefebvre,
J. K. Clegg, J. R. Nitschke* _ **6882 – 6885**

Guanidinium Binding Modulates Guest Exchange within an $[M_4L_6]$ Capsule

---

Anatase TiO_2 nanocrystals have been organized into high-surface-area (150–230 $m^2 g^{-1}$) mesoporous films with long-range chiral nematic ordering. The chiral structure of the anatase films causes them to selectively reflect circularly polarized light and appear iridescent. These materials show replication of structural features found in the silica template on nanometer to millimeter length scales.



Chiral Nanomaterials

K. E. Shopsowitz, A. Stahl, W. Y. Hamad,
M. J. MacLachlan* ________ **6886 – 6890**

Hard Templating of Nanocrystalline Titanium Dioxide with Chiral Nematic Ordering

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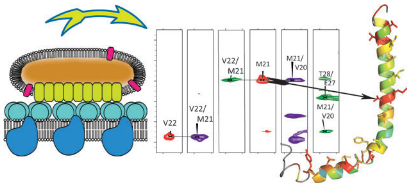


A clever combination: An in situ solid-state NMR analysis of CsmA proteins in the heterogeneous environment of the photoreceptor of *Chlorobaculum tepidum* is reported. Using different combinations of 2D and 3D solid-state NMR spectra, 90% of the CsmA resonances are assigned and provide on the basis of chemical shift data information about the structure and conformation of CsmA in the CsmA–bacteriochlorophyll *a* complex (see picture).

Solid-State NMR Spectroscopy

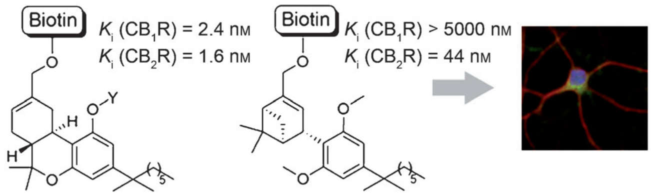
N. V. Kulminskaya, M. Ø. Pedersen,
M. Bjerring, J. Underhaug, M. Miller,
N.-U. Frigaard, J. T. Nielsen,*
N. C. Nielsen* ____________ **6891 – 6895**

In Situ Solid-State NMR Spectroscopy of Protein in Heterogeneous Membranes: The Baseplate Antenna Complex of *Chlorobaculum tepidum*

Small-Molecule Probes

L. Martín-Couce, M. Martín-Fontecha, Ó. Palomares, L. Mestre, A. Cordomí, M. Hernangomez, S. Palma, L. Pardo, C. Guaza, M. L. López-Rodríguez,* S. Ortega-Gutiérrez* ______ **6896 – 6899**

Chemical Probes for the Recognition of Cannabinoid Receptors in Native Systems



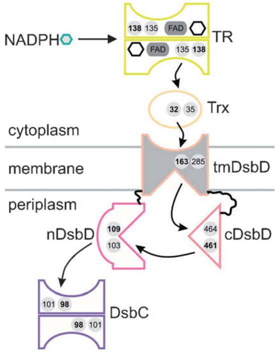
Receptors made visible: The described biotin-tagged small-molecule probes with excellent affinities for the CB$_1$ and CB$_2$ cannabinoid receptors (CB$_1$R and CB$_2$R) enable direct visualization of these receptors in native cellular systems, including neurons (see picture), microglia, and immune cells. This method could overcome some of the limitations of current methodologies and may help to dissect the complexity of the endogenous cannabinoid system.

Enzyme Catalysis

G. Malojčić,* E. R. Geertsma, M. S. Brozzo, R. Glockshuber* ______ **6900 – 6903**

Mechanism of the Prokaryotic Transmembrane Disulfide Reduction Pathway and Its In Vitro Reconstitution from Purified Components

Making your (Dsb) connection: The redox pathway bringing reducing equivalents from bacterial cytoplasm, across the inner membrane, to the three reductive Dsb pathways in the otherwise oxidizing periplasm (see scheme; TR = thioredoxin reductase, Trx = thioredoxin) is reconstituted from purified components. Transfer of reducing equivalents across the membrane is demonstrated and underlying mechanistic details are revealed.

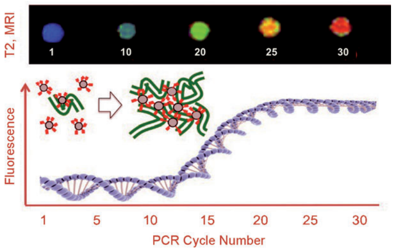


Imaging Agents

D. Alcantara, Y. Guo, H. Yuan, C. J. Goergen, H. H. Chen, H. Cho, D. E. Sosnovik, L. Josephson* ______ **6904 – 6907**

Fluorochrome-Functionalized Magnetic Nanoparticles for High-Sensitivity Monitoring of the Polymerase Chain Reaction by Magnetic Resonance

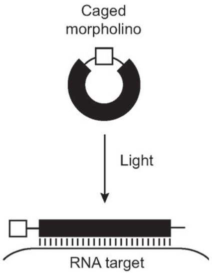
Easy to find: Magnetic nanoparticles bearing fluorochromes (red) that intercalate with DNA (green) form microaggregates with DNA generated by the polymerase chain reation (PCR). These aggregates can be detected at low cycle numbers by magnetic resonance (MR).



Gene Silencing

S. Yamazoe, I. A. Shestopalov, E. Provost, S. D. Leach, J. K. Chen* ____ **6908 – 6911**

Cyclic Caged Morpholinos: Conformationally Gated Probes of Embryonic Gene Function

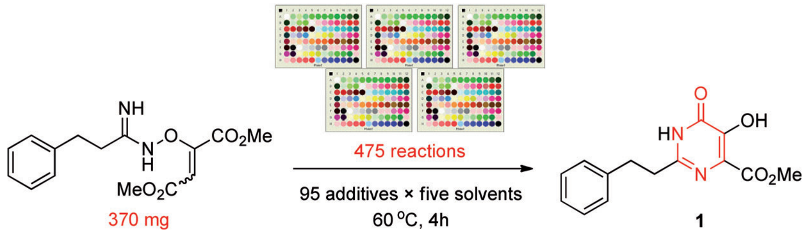


Feeling a bit cagey: Morpholino-based antisense reagents have been caged through oligonucleotide cyclization (see scheme), enabling photocontrol of gene expression in zebrafish embryos and larvae. Using these reagents, the timing of exocrine cell fate commitment in the developing pancreas has been examined.

High-Throughput Screening

A. Bellomo, N. Celebi-Olcum, X. Bu, N. Rivera, R. T. Ruck, C. J. Welch, K. N. Houk,* S. D. Dreher* **6912 – 6915**

Rapid Catalyst Identification for the Synthesis of the Pyrimidinone Core of HIV Integrase Inhibitors

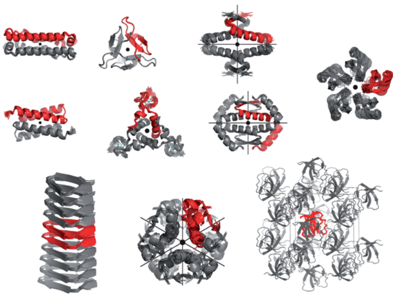


A microscale chemistry improvement engine: A pre-dosed microscale high-throughput experimentation additives platform enables rapid, serendipitous reaction improvement. This platform allowed one chemist to set up 475 experiments and analyze the results using MISER chromatography in a single day, thus resulting in two high-quality catalytic systems for the construction of the title compound **1**. Support for a single-electron transfer mechanism was obtained.

Structure Modeling

B. Bardiaux, B.-J. van Rossum, M. Nilges,* H. Oschkinat* **6916 – 6919**

Efficient Modeling of Symmetric Protein Aggregates from NMR Data

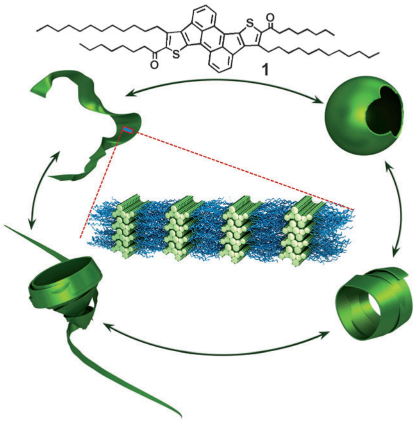


An efficient approach to determine the structures of symmetric protein aggregates from liquid and solid-state NMR data is presented. Any symmetry can be used (cyclic or dihedral point symmetries, helical symmetries, crystallographic symmetries). Because the starting point is the random structure of the monomer, the knowledge of the 3D structure of the monomer is not required.

Self-Assembly

M. Wang, A. R. Mohebbi, Y. Sun, F. Wudl* **6920 – 6924**

Ribbons, Vesicles, and Baskets: Supramolecular Assembly of a Coil–Plate–Coil Emeraldicene Derivative

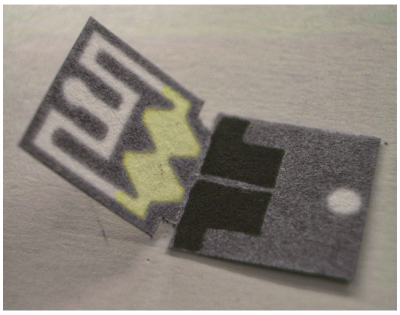


Concentration matters: The self-assembly of title compound **1** evolves from well-defined ribbons to vesicles to baskets (see picture), upon simply decreasing the concentration of **1** in tetrahydrofuran. Electron microscopy revealed a unique self-assembled structure: baskets are formed by curved and self-wrapped nanometer-thin ribbons. The self-assembly of π-conjugated molecule **1** enables to construct nano/micro structures with desired optoelectronic properties.

Biosensors

H. Liu, Y. Xiang, Y. Lu, R. M. Crooks* **6925 – 6928**

Aptamer-Based Origami Paper Analytical Device for Electrochemical Detection of Adenosine

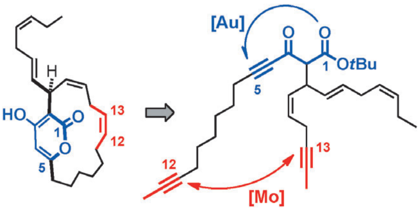


Paper biosensors: An origami sensor is printed on a single piece of paper, folded into a three-dimensional fluidic device, and encapsulated by thermal lamination. Aptamer is trapped in the fluidic channel, where it binds to the target and releases an enzyme to generate a signal. The device is read out using a digital multimeter.

VIP

Natural Product Synthesis

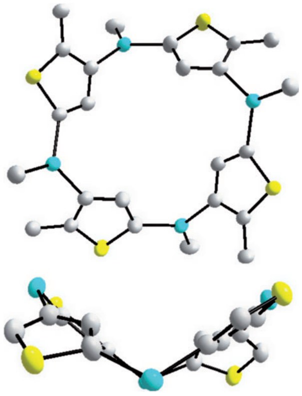
Total Synthesis of Neurymenolide A Based on a Gold-Catalyzed Synthesis of 4-Hydroxy-2-pyrones



Treat me gently: For a selective synthesis of the unusually sensitive cyclophanic α-pyrone neurymenolide A, the chosen catalysts must be able to distinguish between six different sites of unsaturation, without scrambling any of the skipped π systems. This challenge was met with a new gold-catalyzed pyrone synthesis in combination with a molybdenum-catalyzed ring-closing alkyne metathesis.

Supramolecular Metallocycle

Dizincation of a 2-Substituted Thiophene: Constructing a Cage with a [16]Crown-4 Zincocyclic Core

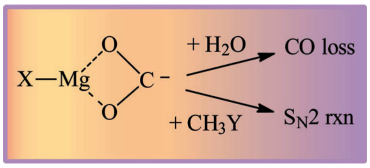


Metal detector: A bowl-shaped nanomolecule (see picture; S yellow, C gray, Zn blue) containing an unprecedented 16-atom $[ZnC_3]_4$ "anti-crown" ring has been unearthed by isolating a dizincated 2-substituted thiophene intermediate that would normally be hidden in tandem functionalization methodology.

Reaction Intermediates

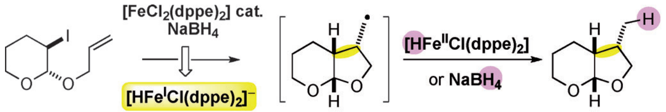
Formation and Characterization of Gaseous Adducts of Carbon Dioxide to Magnesium, $(CO_2)MgX^-$ (X = OH, Cl, Br)

A good fix: The structure and chemical reactivity of a reduced form of CO_2 bonded to magnesium, $XMg(\eta^2\text{-}O_2C)^-$, is reported. Upon reaction with water it loses CO, while it adds CH_3 upon reaction with alkyl halides, thereby signifying nucleophilicity of the carbon atom in $XMg(\eta^2\text{-}O_2C)^-$ in S_N2 reactions.



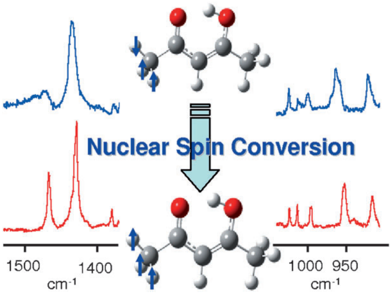
Iron Catalysis

Iron-Catalyzed Reductive Radical Cyclization of Organic Halides in the Presence of $NaBH_4$: Evidence of an Active Hydrido Iron(I) Catalyst



Iron made'em: Iron(II) complexes such as $FeCl_2$ and $[FeCl_2(dppe)_2]$ (dppe = 1,2-bis-diphenylphosphinoethane) are efficient precatalysts for the radical cyclization of unsaturated iodides and bromides in the presence of $NaBH_4$ (see scheme). Cyclic voltammetry studies suggests that the reaction occurs through a radical mechanism via an anionic hydrido iron(I) species as the key intermediate for the activation of the substrates by electron transfer.

A noteworthy example of a molecule with coupled large-amplitude motions is provided by acetylacetone (methyl group torsions and intramolecular hydrogen bonds). The molecule was trapped in solid parahydrogen to investigate the complex proton tunneling processes. Nuclear spin conversion in methyl groups is observed and, combined with IR spectra, documents the coupling between high frequency modes and large amplitude motions.



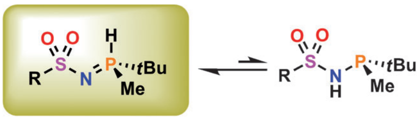
Molecular Dynamics

R. R. Lozada-Garcia, J. Ceponkus, M. Chevalier, W. Chin, J.-M. Mestdagh, C. Crépin* ______ **6947 – 6950**

Nuclear Spin Conversion to Probe the Methyl Rotation Effect on Hydrogen-Bond and Vibrational Dynamics

---

Have a good SIP: P-stereogenic secondary iminophosphorane (SIP) ligands with a sulfonyl group attached to nitrogen have been prepared. In the presence of rhodium, the tautomeric equilibrium is shifted from the favored PH tautomer towards the P^{III} tautomer, thereby allowing coordination of the SIP ligand through the P and O atoms. The resulting Rh complexes are effective in the [2+2+2] cycloaddition of enediynes with terminal alkynes.



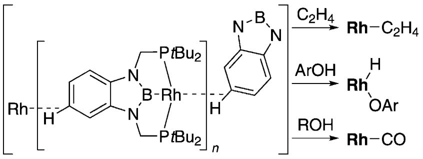
Configurationally and air stable

Phosphorus Ligands

T. León, M. Parera, A. Roglans, A. Riera,* X. Verdaguer* ______ **6951 – 6955**

P-Stereogenic Secondary Iminophosphorane Ligands and Their Rhodium(I) Complexes: Taking Advantage of NH/PH Tautomerism

Front Cover



A little help from my friends: A highly reactive, 16-electron square-planar rhodium complex was isolated. This species displays an intermolecular interaction between the rhodium and the C–H bond of another molecule as the fourth ligand to form an infinite network in the crystal lattice. The complex undergoes oxidative addition to the O–H bond of phenol or a primary alkyl alcohol to give the corresponding hydrido-phenoxido Rh^{III} complex or carbonyl Rh^{I} complex, respectively.

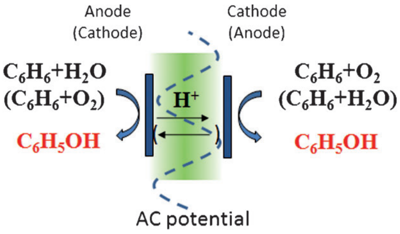
Rhodium Chemistry

M. Hasegawa, Y. Segawa, M. Yamashita,* K. Nozaki* ______ **6956 – 6960**

Isolation of a PBP-Pincer Rhodium Complex Stabilized by an Intermolecular C–H σ Coordination as the Fourth Ligand

---

Works both ways: Phenol was produced by both anodic and cathodic benzene oxidations over the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ electrode in an electrochemical cell, thus allowing the use of AC electrolysis for phenol production. AC electrolysis was found to be more efficient and selective toward phenol production than DC electrolysis.



Phenol Synthesis

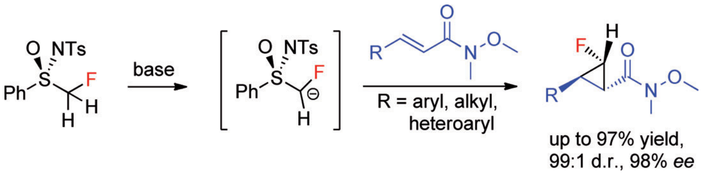
B. Lee, H. Naito, M. Nagao, T. Hibino* ______ **6961 – 6965**

Alternating-Current Electrolysis for the Production of Phenol from Benzene

Cyclopropanation

X. Shen, W. Zhang, L. Zhang, T. Luo,
X. Wan, Y. Gu, J. Hu* ______ **6966 – 6970**

Enantioselective Synthesis of Cyclopropanes That Contain Fluorinated Tertiary Stereogenic Carbon Centers: A Chiral α-Fluoro Carbanion Strategy



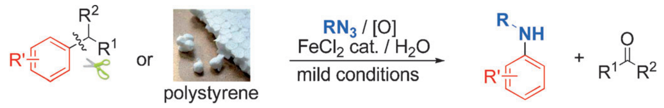
up to 97% yield, 99:1 d.r., 98% *ee*

Chiral transfer: The fluorinated sulfoximine (see scheme; Ts = *p*-toluenesulfonyl) was synthesized and used as the first chiral fluoromethylenation reagent for the synthesis of cyclopropanes that contain fluorinated tertiary stereogenic carbon centers in good yields, good diastereoselectivity, and excellent enantioselectivity.

C–C Cleavage

C. Qin, T. Shen, C. Tang,
N. Jiao* ______ **6971 – 6975**

$FeCl_2$-Promoted Cleavage of the Unactivated C–C Bond of Alkylarenes and Polystyrene: Direct Synthesis of Arylamines



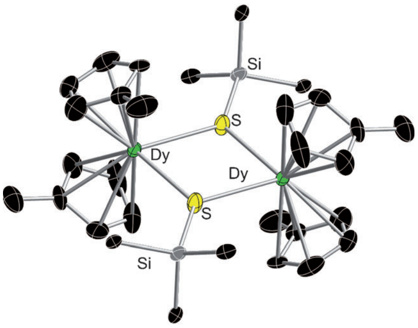
Ironing it out: An efficient and convenient nitrogenation strategy involving C–C bond cleavage for the straightforward synthesis of versatile arylamines is presented. Various alkyl azides and alkylarenes, including the common industrial by-product cumene, react using this protocol. Moreover, this method provides a potential strategy for the degradation of polystyrene.

Single-Molecule Magnets

F. Tuna, C. A. Smith, M. Bodensteiner,
L. Ungur, L. F. Chibotaru, E. J. L. McInnes,
R. E. P. Winpenny, D. Collison,*
R. A. Layfield* ______ **6976 – 6980**

A High Anisotropy Barrier in a Sulfur-Bridged Organodysprosium Single-Molecule Magnet

The sulfur-bridged dimers $[\{Cp'_2Ln(\mu\text{-}SSiPh_3)\}_2]$ (Ln = Gd (**1**), Dy (**2**); Cp′ = η^5-C_5H_4Me) were synthesized by the transmetalation reactions between $[Cp'_3Ln]$ and Ph_3SiSLi. Compound **2** is a single-molecule magnet with slow relaxation of magnetization up to 40 K and an anisotropy barrier of U_{eff} = 133 cm^{-1}. Insight into the SMM properties of **2** and closely related SMMs has been obtained using ab initio calculations.



Energetic Materials

J. D. Moretti,* J. J. Sabatini,*
G. Chen ______ **6981 – 6983**

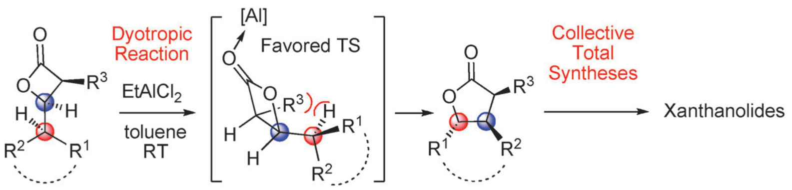
Periodate Salts as Pyrotechnic Oxidizers: Development of Barium- and Perchlorate-Free Incendiary Formulations

In a flash: Pyrotechnic incendiary formulations with good stabilities toward various ignition stimuli have been developed without the need for barium or perchlorate oxidizers. KIO_4 and $NaIO_4$ were introduced as pyrotechnic oxidizers and exhibited excellent pyrotechnic performance. The periodate salts may garner widespread use in military and civilian fireworks because of their low hygroscopicities and high chemical reactivities.

Natural Product Synthesis

W. Ren, Y. Bian, Z. Zhang, H. Shang, P. Zhang, Y. Chen, Z. Yang,* T. Luo,* Y. Tang* ——— **6984 – 6988**

Enantioselective and Collective Syntheses of Xanthanolides Involving a Controllable Dyotropic Rearrangement of *cis*-β-Lactones

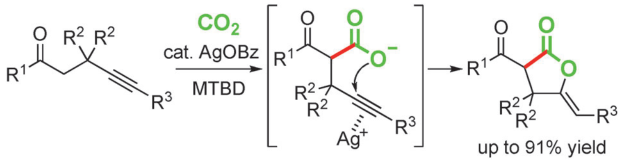


Let's swap: A scalable, atom-economic, enantio-, and diastereoselective synthetic route to trisubstituted γ-butyrolactones based on a Wagner–Meerwein-type dyotropic rearrangement of *cis*-β-lactones is described (see scheme). This methodology was applied in efficient and protecting-group-free formal syntheses and total syntheses of various xanthanolide natural products.

Silver Catalysis

S. Kikuchi, K. Sekine, T. Ishida, T. Yamada* ——— **6989 – 6992**

C–C Bond Formation with Carbon Dioxide Promoted by a Silver Catalyst

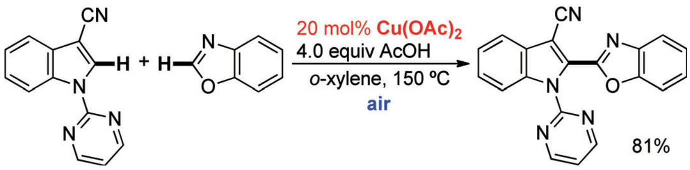


A catalytic amount of silver benzoate with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) was an effective catalytic system for the reaction of carbon dioxide with various ketones containing an alkyne group at an appropriate position (see scheme). These reactions afforded the corresponding γ-lactone derivatives in good to high yields under mild conditions.

Synthetic Methods

M. Nishino, K. Hirano,* T. Satoh, M. Miura* ——— **6993 – 6997**

Copper-Mediated and Copper-Catalyzed Cross-Coupling of Indoles and 1,3-Azoles: Double C–H Activation



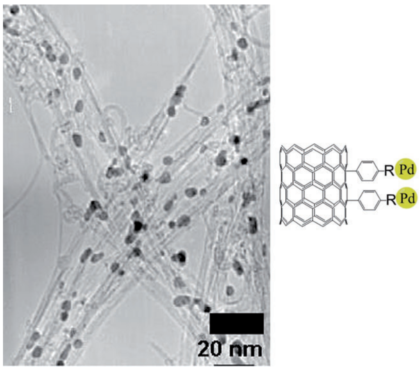
A new bronze age: The described copper-mediated cross-coupling with double C–H activation can provide a convergent access to indole-containing biheteroaryls that are of high interest in pharmaceutical and medicinal chemistry. In this strategy an easily attachable and detachable 2-pyrimidyl directing group is used. Moreover, a variant that is catalytic in copper is achieved by using atmospheric oxygen as an ideal co-oxidant (see scheme).

Fuel-Cell Catalysts

P. Luksirikul, K. Tedsree, M. G. Moloney, M. L. H. Green, S. C. E. Tsang* ——— **6998 – 7001**

Electron Promotion by Surface Functional Groups of Single Wall Carbon Nanotubes to Overlying Metal Particles in a Fuel-Cell Catalyst

A remarkable promotion: Functional groups added onto single-wall carbon nanotubes (SWNTs) can significantly influence the activity of a noble metal for formic acid oxidation. Phenolate groups on SWNTs under alkaline conditions can double the activity of 20% w/w Pd compared to unmodified SWNTs. This catalyst has 14 times higher activity than the commercial benchmark catalyst (10% w/w Pd on Vulcan).

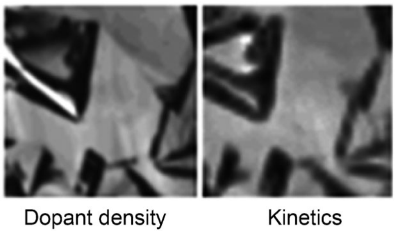


Electrochemical Imaging

H. V. Patten, K. E. Meadows, L. A. Hutton, J. G. Iacobini, D. Battistel, K. McKelvey, A. W. Colburn, M. E. Newton, J. V. Macpherson,* P. R. Unwin* ______ 7002 – 7006

Electrochemical Mapping Reveals Direct Correlation between Heterogeneous Electron-Transfer Kinetics and Local Density of States in Diamond Electrodes

Conducting carbon materials: A multi-microscopy approach shows that local heterogeneous electron-transfer rates at conducting diamond electrodes correlate with the local density of electronic states. This model of electroactivity is of considerable value for the rational design of conducting diamond electrochemical technologies, and also provides key general insights on electrode structure controls in electrochemical kinetics (see picture).

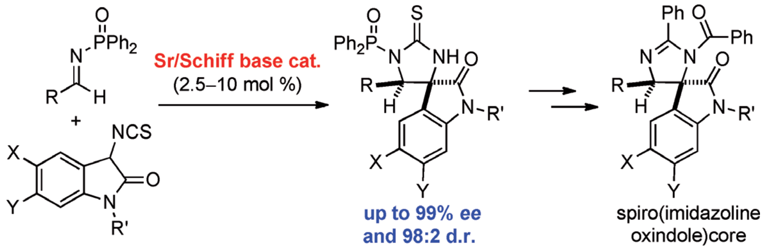


Inside Back Cover

Asymmetric Catalysis

S. Kato, T. Yoshino, M. Shibasaki, M. Kanai,* S. Matsunaga* _ 7007 – 7010

Catalytic Asymmetric Synthesis of Spirooxindoles by a Mannich-Type Reaction of Isothiocyanato Oxindoles



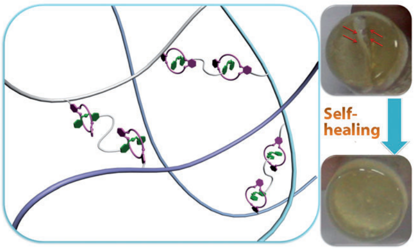
Easy access: A strontium/Schiff base complex as catalyst for the title reaction provided straightforward access to enantiomerically enriched spiro[imidazolidine-4,3′-oxindole] compounds, as well as a spiro[imidazoline-4,3′-oxindole] through a two-step conversion from the Mannich adduct.

Supramolecular Chemistry

M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng, F. Huang* ______ 7011 – 7015

Self-Healing Supramolecular Gels Formed by Crown Ether Based Host–Guest Interactions

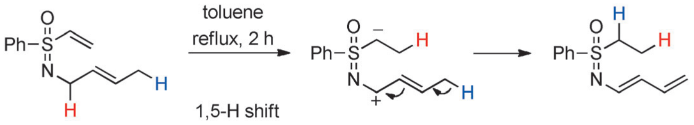
Automatic repair: A polymer with pendent dibenzo[24]crown-8 units (purple in picture) was cross-linked by two bisammonium salts (green) to form two supramolecular gels based on host–guest interactions. These two gels are stimuli-responsive materials that respond to changes of the pH value and are also self-healing materials, as can be seen by eye and as evidenced by rheological data.



Hydrogen Transfer

X. Gao, V. Gaddam, E. Altenhofer, R. R. Tata, Z. Cai, N. Yongpruksa, A. K. Garimallaprabhakaran, M. Harmata* ______ 7016 – 7019

C–H Activation in S-Alkenyl Sulfoximines: An Endo 1,5-Hydrogen Migration



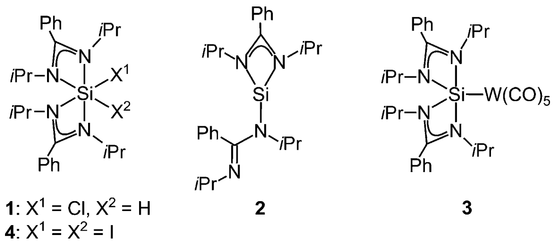
Intramolecular redox reaction: Heating N-alkyl, N-allyl-, and N-benzyl-substituted S-alkenyl sulfoximines under appropriate conditions results in the formation of NH-S-alkyl sulfoximines. The intramolecular redox reaction involves a hydride transfer that occurs by a 6-*endo*-trig process. The intermediates in the reaction can also give access to four- and six-membered heterocyclic rings and a new class of chiral dienes.

Inside Cover

Silicon Chemistry

K. Junold, J. A. Baus, C. Burschka,
R. Tacke* **7020–7023**

Bis[*N*,*N*′-diisopropylbenzamidinato(−)]-silicon(II): A Silicon(II) Compound with Both a Bidentate and a Monodentate Amidinato Ligand



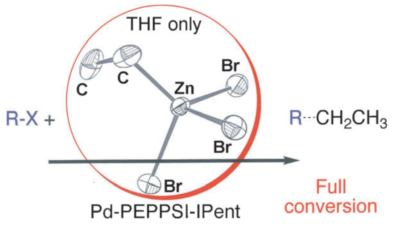
Well looked-after: Reductive HCl elimination of the λ^6-silicon(IV) complex **1** leads to the λ^3-silicon(II) species **2**, a novel type of donor-stabilized silylene. Reaction of **2** with [W(CO)$_6$] and with I$_2$ yields the λ^5-silicon(II) complex **3** and the λ^6-silicon(IV) complex **4**, respectively.

Zincates

L. C. McCann, H. N. Hunter,
J. A. C. Clyburne,
M. G. Organ* **7024–7027**

Higher-Order Zincates as Transmetalators in Alkyl–Alkyl Negishi Cross-Coupling

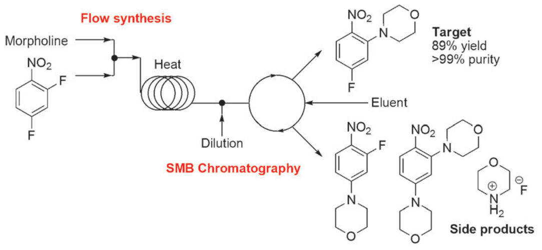
Negishi revisited: Higher-order alkyl zincates have been subjected to Negishi coupling with alkyl bromides. For the first time, coupling takes place in straight THF, i.e., without a salt additive and a high dielectric co-solvent. This provides evidence that it is the higher-order zincate that undergoes transmetalation to Pd, and not mono-anionic zincates or any of the other species present in the Schlenk equilibrium.



Flow Chemistry

A. G. O'Brien, Z. Horváth, F. Lévesque,
J. W. Lee, A. Seidel-Morgenstern,
P. H. Seeberger* **7028–7030**

Continuous Synthesis and Purification by Direct Coupling of a Flow Reactor with Simulated Moving-Bed Chromatography

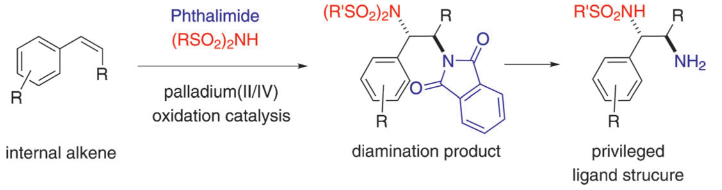


Continuous synthesis meets continuous purification to produce pure products from crude reaction mixtures. In the nucleophilic aromatic substitution of 2,4-difluoronitrobenzene with morpholine the desired monosubstituted product can be continuously separated from the byproducts in a purity of over 99% by coupling a flow reactor to a simulated moving bed (SMB) chromatography module (see scheme).

Palladium Catalysis

C. Martínez, K. Muñiz* **7031–7034**

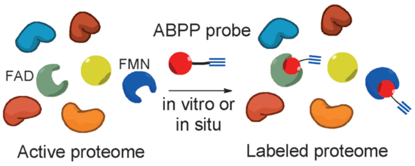
Palladium-Catalyzed Vicinal Difunctionalization of Internal Alkenes: Diastereoselective Synthesis of Diamines



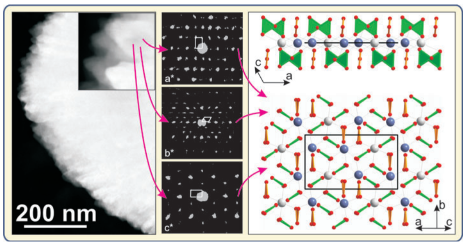
Internal affairs: The first general palladium-catalyzed intermolecular diamination of internal alkenes employs different nitrogen sources, which add to the alkene in a regio- and diastereoselective fashion. The resulting diamination products can be converted directly into a known ligand motif.

Proteomics

High profile: New activity-based protein profiling (ABPP) probes have been designed that target exclusively monoamine oxidases A and B within living cells (see picture; FAD = flavin adenine dinucleotide, FMN = flavin monodinucleotide). With these probes it could be shown that the MAO inhibitor deprenyl, which is in clinical use against Parkinson's disease, shows unique protein specificity despite its covalent mechanism of action.



Vaterite Structure



“**This is a mineral about which there has been much discussion**” is a typical statement about vaterite in older standard textbooks of inorganic chemistry. This polymorph of $CaCO_3$ was first mentioned by H. Vater in 1897, plays key roles in weathering and biomineralization processes, but occurs only in the form of nanosized crystals, unsuitable for structure determination. Its structure could now be solved by automated electron diffraction tomography from 50 nm sized nanocrystals.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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Angewandte Addendum

While this work was in progress, a team led by Z. Li, P. Conti, and F. Gabbaï reported an alternative approach to [^{18}F]-BODIPY dyes.[1] In the same paper, they also demonstrated the positron emission tomography/fluorescence dual modality imaging capabilities of these radiolabeled dyes.

Synthesis of [^{18}F]BODIPY: Bifunctional Reporter for Hybrid Optical/Positron Emission Tomography Imaging

J. A. Hendricks, E. J. Keliher, D. Wan, S. A. Hilderbrand, R. Weissleder,* R. Mazitschek* ____ **4603–4606**

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

DOI: 10.1002/anie.201107957

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[1] Z. Li, T.-P. Lin, S. Liu, C.-W. Huang, T. W. Hudnall, F. P. Gabbaï, P. S. Conti, *Chem. Commun.* **2011**, *47*, 9324–9326.