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:

*V. Mazumder, M. Chi, K. L. More, S. Sun**
Synthesis and Characterization of Multimetallic Pd/Au and Pd/Au/FePt Core/Shell Nanoparticles

*D. V. Esposito, S. T. Hunt, A. L. Stottlemyer, K. D. Dobson, B. E. McCandless, R. W. Birkmire, J. G. Chen**
Low-Cost Hydrogen-Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide (WC) Substrates

*S.-Y. Moon, J.-S. Bae, E. Jeon, J.-W. Park**
Organic Sol-Gel Synthesis: Solution-Processable Microporous Organic Networks

R. Matsui, K. Seto, K. Fujita, T. Suzuki, A. Nakazaki, S. Kobayashi
Unusually *E*-Selective Ring-Closing Metathesis to Form Eight-Membered Rings

*J. S. Chen, T. Zhu, C. M. Li, X. W. Lou**
Building Hematite Nanostructures Using Oriented Attachment

*S. Sun, G. Zhang, D. Geng, Y. Chen, R. Li, M. Cai, X. Sun**
A Highly Durable Platinum Nanocatalyst for PEM Fuel Cells: Multiarmed Starlike Nanowire Single Crystals

*T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey**
Preparation of a Dihydrogen Complex of Cobalt

*Y. Zhang, G. M. Miyake, E. Y.-X. Chen**
Alane-Based Classical and Frustrated Lewis Pairs in Polymer Synthesis: Rapid Polymerization of Methyl Methacrylate and Naturally Renewable Methylene Butyrolactones to High-Molecular-Weight Polymers

*S. Vellalath, I. Čorić, B. List**
***N*-Phosphinyl Phosphoramide: A Chiral Brønsted Acid Motif for the Direct Asymmetric *N*,*O*-Acetalization of Aldehydes**

Author Profile

"My favorite subjects at school were chemistry and physics. When I wake up I check my e-mails …"
This and more about Hsiang-Rong Tseng can be found on page 9036.

Hsiang-Rong Tseng ______ **9036**

News

J. Sauer

M. Driess

C. N. R. Rao

Liebig Medal: J. Sauer ______ **9037**

Alfred Stock Memorial Prize:
M. Driess ______ **9037**

August Wilhelm von Hofmann Medal:
C. N. R. Rao ______ **9037**

Obituaries

Marc Julia (1922–2010)

J.-C. Chottard, J.-Y. Lallemand, D. Mansuy, J.-N. Verpeaux ______ **9038 – 9039**

Books

Silver in Organic Chemistry

Michael Harmata

reviewed by P. J. Pérez ______ **9040**

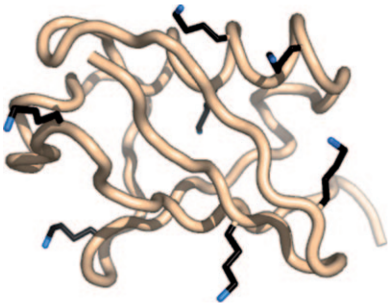
Contents

Highlights

Protein Chemistry

L. J. Martin, R. T. Raines* ____ **9042 – 9044**

Carpe Diubiquitin



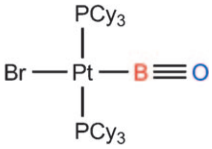
Chained melody: Ubiquitination is forged through the nonstandard isopeptide bond between the ε-nitrogen atom of a lysine residue on a target protein and the C-terminal carboxy group of ubiquitin. Several complementary synthetic approaches have led to designated diubiquitin chains in quantities useful for structure–function analyses, culminating in the total chemical synthesis of all seven diubiquitin chains.

Boron Chemistry

S. A. Westcott* ____ **9045 – 9046**

BO Chemistry Comes Full Circle

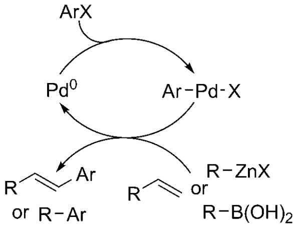
No BO problem! Low-coordinate boron centers can be stabilized by using late transition metals, for example a platinum bisphosphine fragment. $[Pt(PCy_3)_2]$ reacts with $Br_2BOSiMe_3$ to give *trans*-$[(PCy_3)_2PtBr(BO)]$, which contains an unprecedented thermally stable B≡O bond (see picture, Cy = cyclohexyl).



Nobel Prize in Chemistry 2010

X.-F. Wu, P. Anbarasan, H. Neumann, M. Beller* ____ **9047 – 9050**

From Noble Metal to Nobel Prize: Palladium-Catalyzed Coupling Reactions as Key Methods in Organic Synthesis



Building bridges: Palladium-catalyzed cross-coupling reactions of aryl halides and related compounds allow the expeditious and controlled synthesis of important carbon-based scaffolds (see scheme). Their essential role in organic chemistry has resulted in such reactions being recognized by the Nobel Prize for Chemistry 2010.

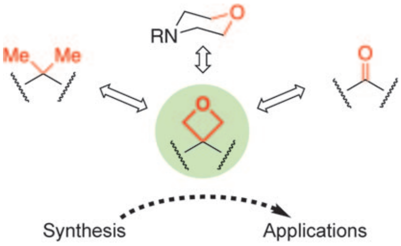
Minireviews

Oxetanes

J. A. Burkhard, G. Wuitschik, M. Rogers-Evans,* K. Müller,* E. M. Carreira* ____ **9052 – 9067**

Oxetanes as Versatile Elements in Drug Discovery and Synthesis

Small but powerful: In recent years oxetanes have received newly gained attention in medicinal chemistry and by the synthetic community since it has been found that the introduction of an oxetane unit in the molecular scaffold of a compound can significantly modify its properties. This Minireview summarizes the advantages of oxetanes in drug discovery and outlines chemical transformations involving oxetanes.



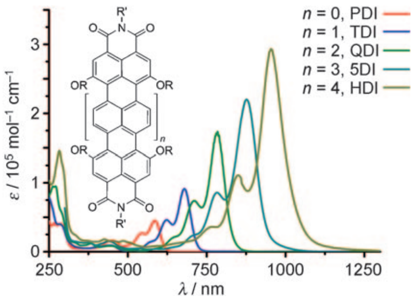
For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. 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$ 9442/8583 (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

Rylene Dyes

T. Weil,* T. Vosch, J. Hofkens,* K. Peneva, K. Müllen* ______ **9068 – 9093**

The Rylene Colorant Family—Tailored Nanoemitters for Photonics Research and Applications

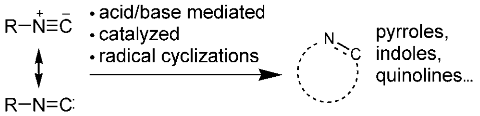


Live and let dye: Rylene dyes, such as those shown in the picture together with their absorption spectra (R = *tert*-octylphenyl, R' = diisopropylphenyl) have outstanding optical properties and can be modified in a site-directed fashion. In recent years, several novel applications of these functional materials have emerged, such as in photonics, single-molecule spectroscopy, as well as for biological investigations.

Synthetic Methods

A. V. Lygin, A. de Meijere* ______ **9094 – 9124**

Isocyanides in the Synthesis of Nitrogen Heterocycles



“Aromatic compounds”: The pungent odor of volatile isocyanides is by far compensated by the unique properties of the isocyano group. Since their discovery some 150 years ago, isocyanides have found numerous applications in the synthesis of nitrogen heterocycles. Apart from various multicomponent processes, many other alternatives exist to build such ring systems from isocyanides.

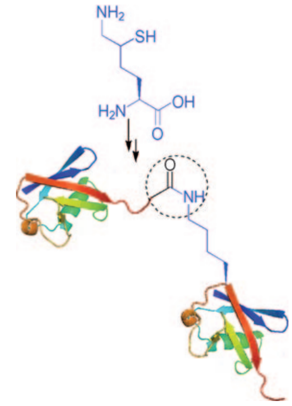
Communications

Protein Synthesis

K. S. A. Kumar, L. Spasser, L. A. Erlich, S. N. Bavikar, A. Brik* ______ **9126 – 9131**

Total Chemical Synthesis of Di-ubiquitin Chains

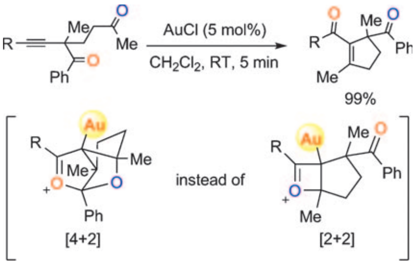
Building the chains: A general and effective approach for the total chemical synthesis of all the di-ubiquitin chains (see picture) is presented. The behavior of the synthetic chains in the presence of isopeptidase T, an enzyme responsible for the disassembly of the majority of unanchored polyubiquitin in vivo, was examined.



Gold Catalysis

L.-P. Liu,* D. Malhotra, R. S. Paton, K. N. Houk,* G. B. Hammond* ______ **9132 – 9135**

The [4+2], not [2+2], Mechanism Occurs in the Gold-Catalyzed Intramolecular Oxygen Transfer Reaction of 2-Alkynyl-1,5-Diketones



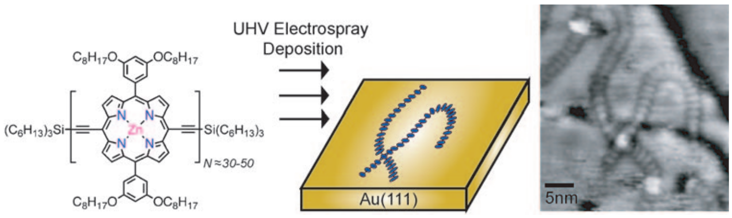
[2+2] or [4+2]? Mechanistic studies on the gold-catalyzed intramolecular oxygen transfer of 2-alkynyl-1,5-diketones were performed using isotopic experiments and quantum chemical calculations. The results demonstrate that the transformation follows a [4+2] pathway instead of the previously proposed [2+2] path (see scheme). Various substrates were employed in the reaction and the corresponding products were obtained in excellent yields.

Contents

Polymers on Surfaces

A. Saywell, J. K. Sprafke, L. J. Esdaile, A. J. Britton, A. Rienzo, H. L. Anderson, J. N. O'Shea, P. H. Beton* — **9136–9139**

Conformation and Packing of Porphyrin Polymer Chains Deposited Using Electrospray on a Gold Surface



Molecular worms: Porphyrin polymers and oligomers are deposited on a Au(111) surface using electrospray deposition and are shown to adopt an arrangement where chains from neighboring molecules are interdigitated. Although the flexible nature of the polymers gives rise to sharp kinks and the crossing of polymer strands (see scheme), a longer correlation length as compared with solvated oligomers is observed.

Living Polymerization

J. Wei, W. Zhang, R. Wickham, L. R. Sita* ——— **9140–9144**

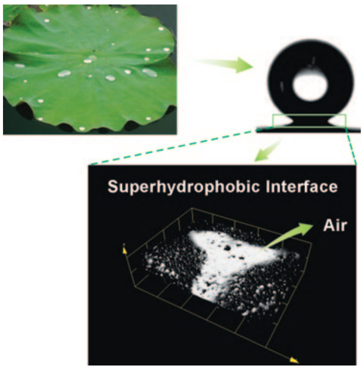
Programmable Modulation of Co-monomer Relative Reactivities for Living Coordination Polymerization through Reversible Chain Transfer between "Tight" and "Loose" Ion Pairs

Not leaving anything to chance: Rapid and reversible exchange between "tight" and "loose" ion pairs was used to modulate the relative reactivities of ethene and 1-hexene or cyclopentene in a programmed fashion for living coordination chain-transfer polymerization. Thus, different grades of a monodisperse polyolefin copolymer, such as the poly(ethene-*co*-1-hexene) samples shown, could be obtained with a single cationic transition-metal catalyst.

Surface Chemistry

C. Luo, H. Zheng, L. Wang, H. Fang, J. Hu, C. Fan,* Y. Cao,* J. Wang* — **9145–9148**

Direct Three-Dimensional Imaging of the Buried Interfaces between Water and Superhydrophobic Surfaces

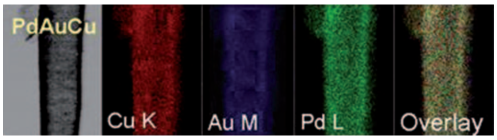


Walking on air: Confocal laser scanning microscopy can be used to provide distinct 3D images of air at buried superhydrophobic interfaces (see picture, bright area). Two hydrophobic states, Wenzel and Cassie states, have been quantitatively visualized and distinctly identified. The 10 μm thick air cushion drastically decreases water adhesion, thus making water droplets roll off the surface and readily remove surface contaminants (self-cleaning).

Fuel Cells

C.-H. Cui, H.-H. Li, J.-W. Yu, M.-R. Gao, S.-H. Yu* ——— **9149–9152**

Ternary Heterostructured Nanoparticle Tubes: A Dual Catalyst and Its Synergistic Enhancement Effects for O_2/H_2O_2 Reduction

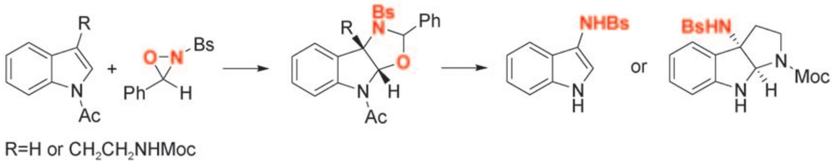


ORR things bright and beautiful: A new kind of unsupported Pd-Au-Cu (PdAuCu) ternary heterostructured nanoparticle-tube catalyst was synthesized (see TEM image and dispersive X-ray spectroscopy maps). The incorporation of Au into a PdCu system gives a synergistic enhancement of the oxygen reduction reaction (ORR) and of the H_2O_2 reduction reaction. The approach provides a promising route to the development of gas/liquid oxidant fuel cells with ultrahigh electrical power output.

Indole Oxidation

T. Benkovics, I. A. Guzei,
T. P. Yoon* ______________ **9153 – 9157**

Oxaziridine-Mediated Oxyamination of Indoles: An Approach to 3-Aminoindoles and Enantiomerically Enriched 3-Aminopyrroloindolines

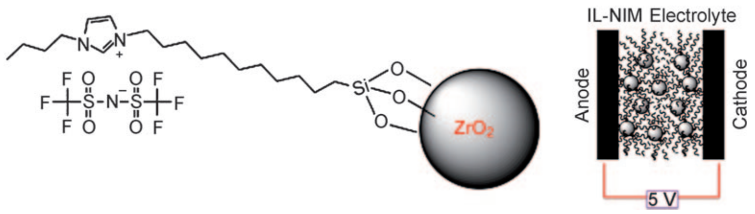


A radical solution: A highly regioselective copper(II)-catalyzed oxyamination of *N*-acyl indoles with oxaziridines gave aminal products that could be converted in a single step into 3-aminoindoles and 3-aminopyrroloindolines (see scheme). When a chiral *N*-acyl group was used, the core fragment of some architecturally fascinating pyrroloindoline alkaloids was formed with 91 % *ee*. Bs = benzenesulfonyl, Moc = methoxycarbonyl.

Lithium Ion Batteries

S. S. Moganty, N. Jayaprakash,
J. L. Nugent, J. Shen,
L. A. Archer* ______________ **9158 – 9161**

Ionic-Liquid-Tethered Nanoparticles: Hybrid Electrolytes

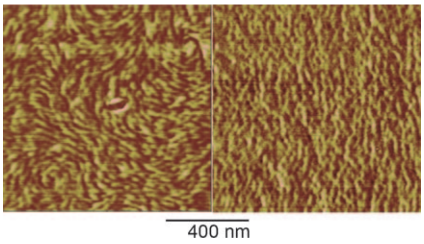


A new class of solventless electrolytes was created by tethering ionic liquids to hard inorganic ZrO_2 nanostructures (see picture; NIM = nanoscale ionic material). These hybrid fluids exhibit exceptional redox stability windows, excellent thermal stability, good lithium transference numbers, long-term interfacial stability in the presence of a lithium anode and, when doped with lithium salt, reasonable ionic conductivities.

Block Copolymers

D. Han, X. Tong, Y. Zhao,
Y. Zhao* ______________ **9162 – 9165**

Block Copolymers Comprising π-Conjugated and Liquid Crystalline Subunits: Induction of Macroscopic Nanodomain Orientation

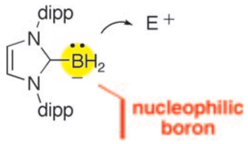


Block party: A block copolymer comprises both regioregular poly(3-hexylthiophene) (P3HT) and a side-chain liquid-crystalline polymer (SCLCP) bearing azobenzene mesogens. The SCLCP block has a clearing temperature above the high crystal-melting temperature of P3HT, therefore surface- and photoinduced orientation of mesogens in the SCLCP block can be used to align stripelike P3HT nanodomains on the macroscopic scale (see picture for AFM images).

N-Heterocyclic Carbenes

J. Monot, A. Solovyev, H. Bonin-Dubarle,
É. Derat, D. P. Curran,* M. Robert,
L. Fensterbank,* M. Malacria,*
E. Lacôte* ______________ **9166 – 9169**

Generation and Reactions of an Unsubstituted N-Heterocyclic Carbene Boryl Anion

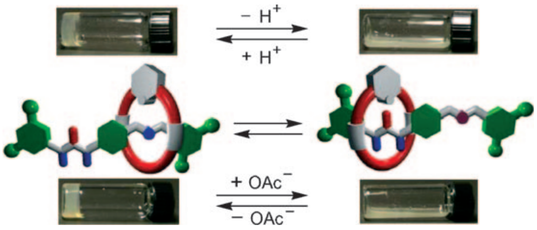


Lying low: A lithiated unsubstituted N-heterocyclic carbene (NHC) boryl anion can be generated by reduction, and trapped by electrophiles (see scheme; dipp = 2,6-diisopropylphenyl) to provide new substituted NHC boranes. It is yet another example of a low-valent boron compound or boron-containing reactive intermediate stabilized by an NHC, thereby extending the scope of NHC borane chemistry.

Molecular Recognition

S.-Y. Hsueh, C.-T. Kuo, T.-W. Lu, C.-C. Lai,
Y.-H. Liu, H.-F. Hsu, S.-M. Peng,
C.-h. Chen,* S.-H. Chiu* ____ **9170–9173**

Acid/Base- and Anion-Controllable Organogels Formed From a Urea-Based Molecular Switch

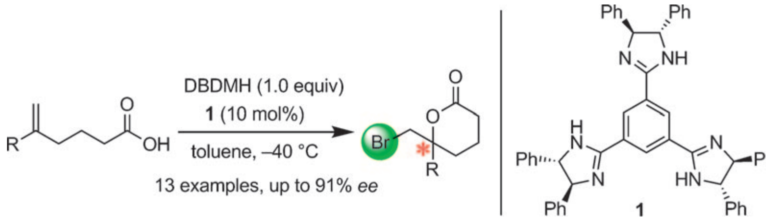


A switch in time: Gel–sol transitions of a urea-based [2]rotaxane gelator are controlled by the degree of solvent exposure of the hydrogen-bond-donating urea station and the orientation of the hydrogen-bond-accepting C=O groups of the interlocked ethylene glycol based macrocycle (N blue, O and macrocycle red, phenyl green). Both acid/base and anion-exchange control can be used to reversibly transition the rotaxane in 1-pentanol between solution and gel states.

Organocatalysis

K. Murai, T. Matsushita, A. Nakamura,
S. Fukushima, M. Shimura,
H. Fujioka* ____ **9174–9177**

Asymmetric Bromolactonization Catalyzed by a C_3-Symmetric Chiral Trisimidazoline

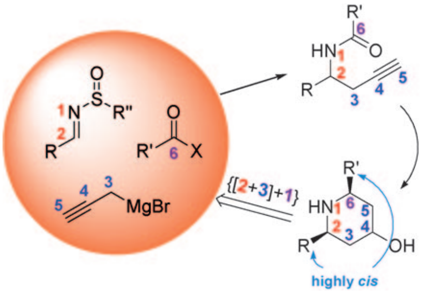


A productive alliance: In an enantioselective organocatalytic bromolactonization of 5-substituted hex-5-enoic acids (see scheme), it appears that the formation of an ion pair through interaction of the trisimidazoline catalyst **1** with the substrate both creates a chiral environment and promotes the cyclization by activating the carboxylic acid. DBDMH = 1,3-dibromo-5,5-dimethylhydantoin.

Nitrogen Heterocycles

L. Cui, C. Li, L. Zhang* ____ **9178–9181**

A Modular, Efficient, and Stereoselective Synthesis of Substituted Piperidin-4-ols

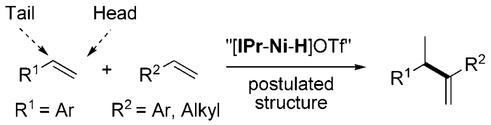


The pied piper-idinol of Hamelin: The one-pot synthesis of piperidin-4-ols by sequential gold-catalyzed cyclization, chemoselective reduction, and spontaneous Ferrier rearrangement has a broad substrate scope and shows excellent diastereoselectivity in the ring-formation step. This chemistry was employed in the six-step enantioselective synthesis of (+)-subcosine II.

Olefination

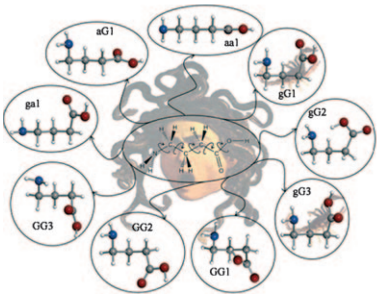
C.-Y. Ho,* L. He ____ **9182–9186**

Catalytic Intermolecular Tail-to-Tail Hydroalkenylation of Styrenes with α Olefins: Regioselective Migratory Insertion Controlled by a Nickel/N-Heterocyclic Carbene



Making head or tail of it: The first single-operation, highly selective intermolecular tail-to-tail hetero-hydroalkenylation from two readily available monosubstituted alkenes is described (see scheme; IPr = 1,3-Bis(2,6-di-isopropylphenyl)imidazol-2-ylidene). The reaction is catalyzed by the proposed [(IPr)NiH]OTf species. The method allows the use of more common and structurally diverse α olefins as substrates, which were previously not compatible with known methods.

Conformation confirmation: The nine conformers of the neurotransmitter γ-aminobutyric acid (GABA) identified in the gas phase can serve as a basis to represent the shape of GABA. An n→π* interaction guided by the Bürgi–Dunitz trajectory of nucleophilic addition is thought to be relevant in the stabilization of two of the folded conformers (**gG1** and **gG3** in the picture).

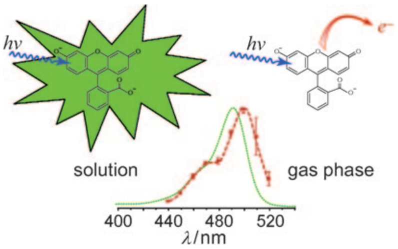


Gas-Phase Conformations

S. Blanco, J. C. López,* S. Mata,
J. L. Alonso ______________ **9187 – 9192**

Conformations of γ-Aminobutyric Acid (GABA): The Role of the n→π* Interaction

---

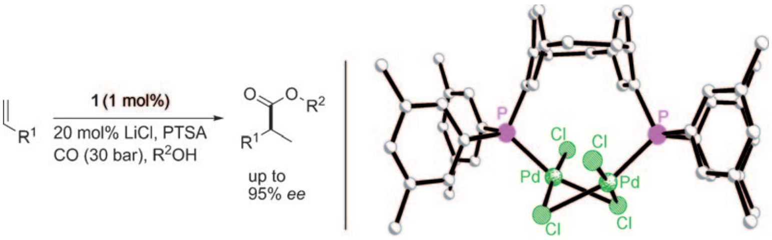


Not so bright: Ion trap mass spectrometry is used in conjunction with optical excitation and detection to study the intrinsic spectroscopic properties of the fluorescein cation, monoanion, and dianion in the gas phase. The dianion, which is a fluorescence quantum yield standard in solution, does not fluoresce significantly in the absence of solvent (see picture) because electron detachment is the favored deactivation pathway in the gas phase.

Spectroscopy

P. D. McQueen, S. Sagoo, H. Yao,
R. A. Jockusch* ______________ **9193 – 9196**

On the Intrinsic Photophysics of Fluorescein



1

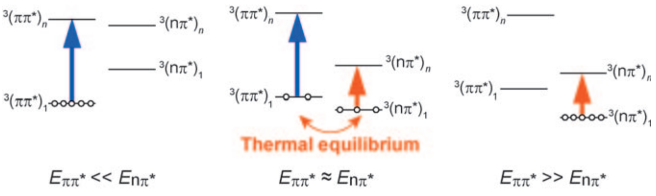
Joined at Pd: Novel palladium catalysts like **1**, in which the planar-chiral phosphine acts as a bridging ligand, have been developed. These dimetallic complexes are highly enantioselective catalysts in the hydroxycarbonylation of alkenes, a reaction that has proven problematic over the years. PTSA = *para*-toluenesulfonic acid.

Enantioselective Carbonylation

T. M. Konrad, J. A. Fuentes,
A. M. Z. Slawin,
M. L. Clarke* ______________ **9197 – 9200**

Highly Enantioselective Hydroxycarbonylation and Alkoxycarbonylation of Alkenes using Dipalladium Complexes as Precatalysts

---



Lay low for a while: The low-lying nπ* and ππ* triplet states of substituted acetophenones have been directly observed by time-resolved near-infrared spectroscopy. The apparent reactivities of the ππ* T_1 states of acetophenones have been shown to arise from the thermal population of the higher nπ* T_2 states. Thermal equilibrium also occurs between the T_1 and T_2 states of the acetophenones.

Photochemistry

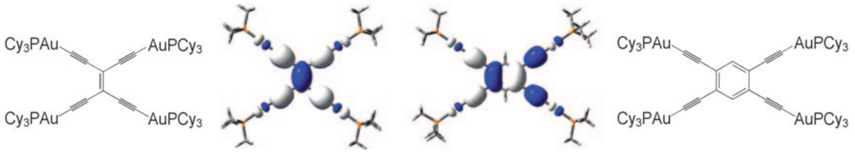
S. Yabumoto, S. Shigeto,* Y.-P. Lee,
H. Hamaguchi* ______________ **9201 – 9205**

Ordering, Interaction, and Reactivity of the Low-Lying nπ* and ππ* Excited Triplet States of Acetophenone Derivatives

Photophysics

G. S. M. Tong,* P. K. Chow,
C.-M. Che* ______________ 9206 – 9209

Where is the Heavy-Atom Effect? Role of the Central Ligand in Tetragold(I) Ethynyl Complexes

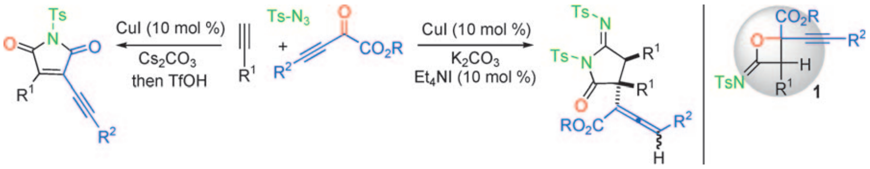


He ain't heavy: The heavy-atom effect is not the sole factor that determines the efficiency of intersystem crossing and triplet radiative decay rates. Theoretical calculations along with experimental evidence show that the central ligand plays a decisive role in the luminescence behavior of tetragold(I) ethynyl complexes (see structures and representations of the highest occupied molecular orbitals).

Heterocycle Synthesis

W. Yao, L. Pan, Y. Zhang, G. Wang,
X. Wang, C. Ma* ___________ 9210 – 9214

Three-Component Assembly and Divergent Ring-Expansion Cascades of Functionalized 2-Iminooxetanes

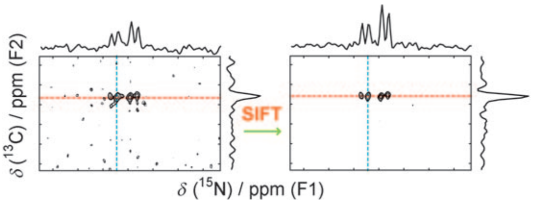


A bold diversification strategy: Aromatic alkynes, *p*-toluenesulfonyl azide, and aromatic 2-oxobut-3-ynoates underwent a copper(I)-catalyzed multicomponent reaction to provide functionalized 2-iminooxetanes **1**, which could be converted selectively into five-membered nitrogen-containing heterocycles of two different sorts, depending on the reaction conditions (see scheme; Tf = trifluoromethanesulfonyl; R = Et, *i*Pr).

Solid-State NMR Spectroscopy

Y. Matsuki, M. T. Eddy, R. G. Griffin,
J. Herzfeld* _______________ 9215 – 9218

Rapid Three-Dimensional MAS NMR Spectroscopy at Critical Sensitivity

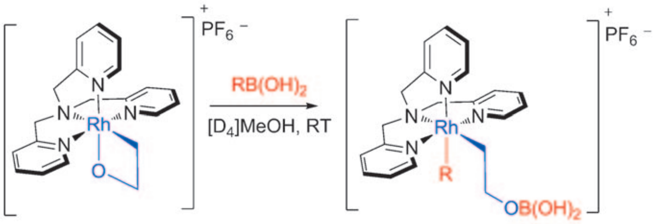


Sensitive SIFTing: Multidimensional nonuniform sampling (NUS) NMR spectroscopy is extended to the severely sensitivity-limited regime typical of MAS NMR of biomacromolecules by the use of spectroscopy by the integration of frequency and time domain information (SIFT). A three-dimensional MAS NMR experiment is expedited (here 3.4-fold) without losing sensitivity or resolution.

Olefin Functionalization

A. Dauth, J. A. Love* _______ 9219 – 9224

Strategy Towards Olefin Carbohydroxylation: Transmetalation of 2-Rhodaoxetanes with Organoboron Nucleophiles



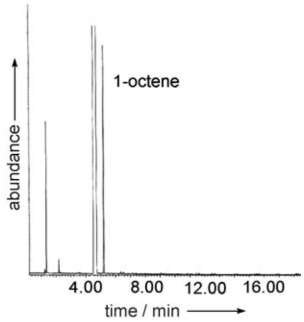
Taking the first step: A 2-rhodaoxetane undergoes efficient transmetalation with a variety of functionalized aryl- and alkenyl boronic acids (see scheme). This process exhibits excellent functional-group compatibility and constitutes the first step in a proposed catalytic oxidative olefin functionalization.

Catalyst Design

S. Licciulli, I. Thapa, K. Albahily, I. Korobkov, S. Gambarotta,* R. Duchateau,* R. Chevalier, K. Schuhen ______ 9225 – 9228

Towards Selective Ethylene Tetramerization

And the magic number is … 4! A large amount of oligomer-free 1-octene (99.9%) was produced from ethylene by a catalytic system based on chromium during the formation of polyethylene wax [see GC–MS chromatogram; the other three significant peaks are methanol (quenching agent), ethyl acetate (needle-rinsing agent), and toluene (solvent)].

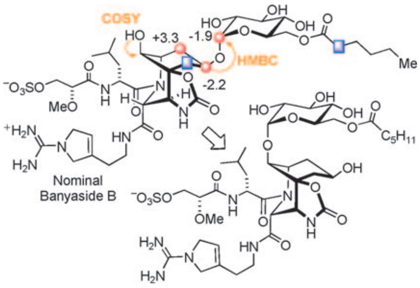


Natural Product Synthesis

C. S. Schindler, L. Bertschi, E. M. Carreira* ______ 9229 – 9232

Total Synthesis of Nominal Banyaside B: Structural Revision of the Glycosylation Site

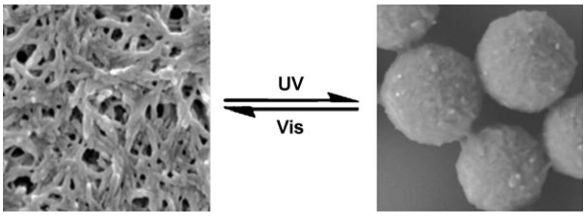
The total synthesis of the tripeptide nominal banyaside B relies on nonstandard peptide-bond-forming reactions. A key outcome of these synthetic studies is the proposal of a revised structure for natural banyaside B, in which the glycoside is indeed linked to the Abn core at the axial C-9 OH and not C-7 as in nominal banyaside B.



Polyoxometalates

Y. Yan, H. Wang, B. Li, G. Hou, Z. Yin, L. Wu,* V. W. W. Yam ______ 9233 – 9236

Smart Self-Assemblies Based on a Surfactant-Encapsulated Photoresponsive Polyoxometalate Complex



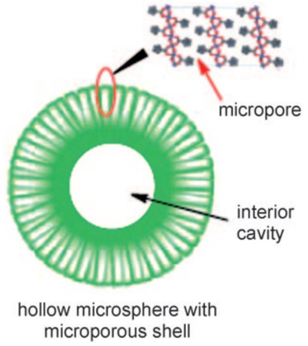
Smart POMs: A surfactant-encapsulated organic-grafted polyoxometalate (POM) is synthesized by grafting a photoresponsive azobenzene group to an Anderson-type POM cluster. Self-assemblies of the hybrid complexes exhibit photocontrolled reversible aggregation and morphological change as a result of photoisomerization-induced structural alternation (see figure).

Hollow Microspheres

J. Huo, L. Wang,* E. Irran, H. J. Yu, J. M. Gao, D. S. Fan, B. Li, J. J. Wang, W. B. Ding, A. M. Amin, C. Li, L. Ma ______ 9237 – 9241

Hollow Ferrocenyl Coordination Polymer Microspheres with Micropores in Shells Prepared by Ostwald Ripening

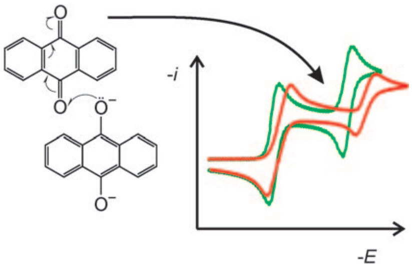
From the inside out: Hollow ferrocenyl coordination polymer microspheres with microporous shells were prepared by a convenient and template-free approach. An Ostwald ripening mechanism is responsible for the formation of hollow cavities. The hierarchically hollow coordination polymer microspheres have potential applications in catalysis, drug delivery, and hydrogen storage.



Voltammetry

S. R. Belding, J. G. Limon-Petersen,
E. J. F. Dickinson,
R. G. Compton* ———— **9242–9245**

Cyclic Voltammetry in the Absence of Excess Supporting Electrolyte Offers Extra Kinetic and Mechanistic Insights: Comproportionation of Anthraquinone and the Anthraquinone Dianion in Acetonitrile

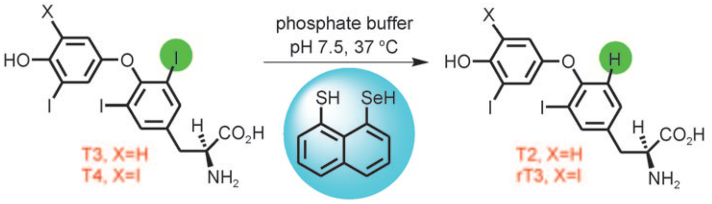


Less is more: The use of voltammetry in the total or partial absence of supporting electrolyte provides kinetic and mechanistic information beyond that available from familiar fully supported voltammetry. For example, unsupported voltammetry demonstrates that the comproportionation of anthraquinone and anthraquinone dianion proceeds at a diffusionally controlled rate in acetonitrile, a result which could not be determined from "diffusion-only" voltammetry.

Enzyme Mimics

D. Manna, G. Mugesh* —— **9246–9249**

A Chemical Model for the Inner-Ring Deiodination of Thyroxine by Iodothyronine Deiodinase

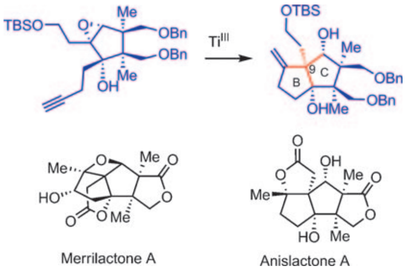


The I of the beholder: The presented chemical model for the inner-ring deiodination of thyroxine (T4) and 3,5,3′-triiodothyronine (T3) by iodothyronine deiodinase (see scheme) highlights the importance of an in-built thiol group in proximity to the selenium atom. The effective removal of iodine in the case of T4 indicates that an enol–keto tautomerism is not required for deiodination.

Natural Products

L. Shi, K. Meyer,
M. F. Greaney* ———— **9250–9253**

Synthesis of (±)-Merrilactone A and (±)-Anislactone A

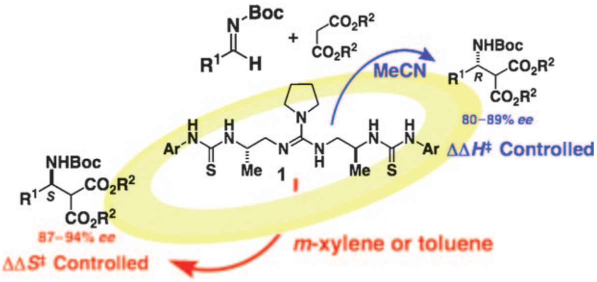


A concise synthesis of each of the sesquiterpenoids merrilactone A and anislactone A is described using a common route. Reductive cleavage of an epoxide using Ti^{III} and radical cyclization is used to install the C9 quaternary center at the heart of the BC bicycle (see scheme). Selective lactonization sequences then define regiodivergent pathways to both merrilactone A (formal synthesis) and anislactone A (total synthesis).

Synthetic Methods

Y. Sohtome,* S. Tanaka,
K. Takada, T. Yamaguchi,
K. Nagasawa* ———— **9254–9257**

Solvent-Dependent Enantiodivergent Mannich-Type Reaction: Utilizing a Conformationally Flexible Guanidine/Bisthiourea Organocatalyst

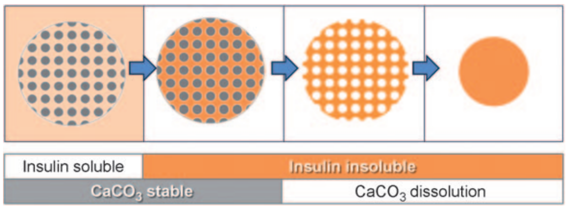


Flex control: Malonate and *tert*-butoxycarbonyl (Boc)-protected imines react in the presence of the flexible catalyst **1** to furnish the *S* or the *R* adduct depending upon the solvent used. Kinetic analyses in this enantiodivergent organocatalysis show that enthalpy–entropy compensation explains this behavior.

Protein Microspheres

D. V. Volodkin,* R. von Klitzing,
H. Möhwald ———— **9258 – 9261**

Pure Protein Microspheres by Calcium Carbonate Templating



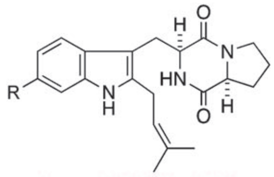
Swapping spheres: Monodisperse protein microspheres can be fabricated by templating on porous CaCO$_3$ microcores (see picture; CaCO$_3$ gray, insulin orange). The CaCO$_3$ cores decompose upon variation of pH from 9.0 to 5.0, whereas the insulin model protein precipitates. The method requires mild conditions, no additives, and minimal processing.

Natural Products Synthesis

T. Yamakawa, E. Ideue, J. Shimokawa,
T. Fukuyama* ———— **9262 – 9265**

Total Synthesis of Tryprostatins A and B

A reasonable approach to the radical: The establishment of reliable conditions for the radical-mediated construction of indoles enabled the highly efficient synthesis of tryprostatins A and B. Use of the radical initiator 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) has allowed to carry out the radical cyclization at just 30 °C, thereby suppressing the formation of byproducts.



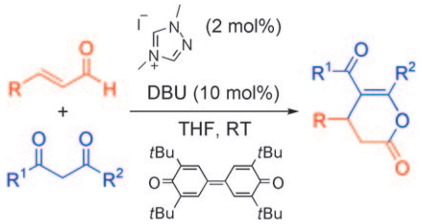
tryprostatin R: X = MeO
tryprostatin R: X = H

Organocatalysis

S. De Sarkar, A. Studer* ——— **9266 – 9269**

NHC-Catalyzed Michael Addition to α,β-Unsaturated Aldehydes by Redox Activation

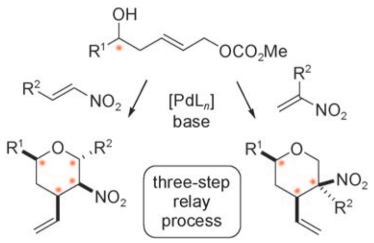
Through oxidative carbene catalysis the reactivity of enals can be reversed at the β position from the typical electrophilic to nucleophilic (homoenolate chemistry) further to electrophilic reactivity by two consecutive umpolung processes. These redox-activated Michael acceptors show higher reactivity at the β position than that for the starting enals. Their reactions with β-dicarbonyl compounds provide dihydropyranones in good to excellent yields under mild conditions.



Domino Reactions

L. Wang, P. Li, D. Menche* **9270 – 9273**

Concise Synthesis of Tetrahydropyrans by a Tandem Oxa-Michael/Tsuji–Trost Reaction

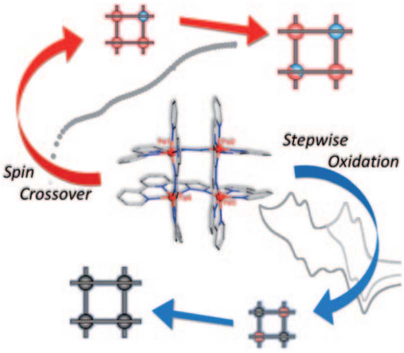


A novel domino sequence facilitates the rapid assembly of polysubstituted tetrahydropyrans. The one-pot relay process generates up to three new stereogenic centers, including a tetrasubstituted carbon center, in a highly concise and convergent fashion from simple starting materials.

Molecular Switches

B. Schneider, S. Demeshko, S. Dechert,
F. Meyer* **9274 – 9277**

A Double-Switching Multistable Fe$_4$ Grid Complex with Stepwise Spin-Crossover and Redox Transitions



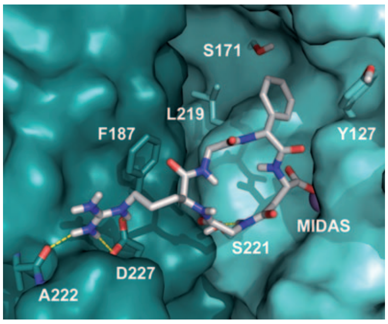
Gridlock! A [2×2] Fe$_4$ grid complex (see picture) with unprecedented stability features two orthogonal switching modes: spin-crossover and redox processes. Oxidation also switches between antiferromagnetic and ferromagnetic coupling. The [HS-LS-HS-LS] Fe$^{II}_4$ and [Fe$^{II}_2$Fe$^{III}_2$] forms are both twofold degenerate, with identical metal ions located at diagonal vertices of the grid, making the system an attractive component for quantum cellular automata.

Peptidic Inhibitors

A. O. Frank, E. Otto, C. Mas-Moruno,
H. B. Schiller, L. Marinelli, S. Cosconati,
A. Bochen, D. Vossmeyer, G. Zahn,
R. Stragies, E. Novellino,
H. Kessler* **9278 – 9281**

Conformational Control of Integrin-Subtype Selectivity in *iso*DGR Peptide Motifs: A Biological Switch

The rearrangement of asparagine to isoaspartate (*iso*D) is responsible for the deactivation of many functional proteins. However, the *iso*DGR motif, which is optimally presented as a conformationally controlled cyclic pentapeptide, binds selectively to $\alpha5\beta1$ integrin (see the docking model) with an affinity comparable to that of the peptidic antitumor agent Cilengitide.

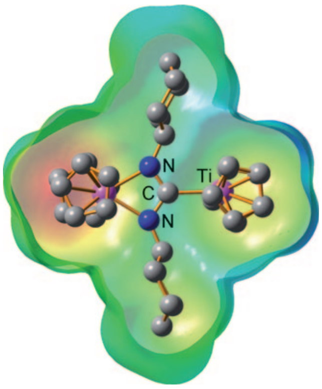


Titanocene Carbene

O. Theilmann, M. Ruhmann, A. Villinger,
A. Schulz,* W. W. Seidel, K. Kaleta,
T. Beweries, P. Arndt,
U. Rosenthal* **9282 – 9285**

[Cp$_2$Ti^{III}(NCy)$_2$C–Ti^{III}Cp$_2$]: A Transient Titanocene Carbene Complex?

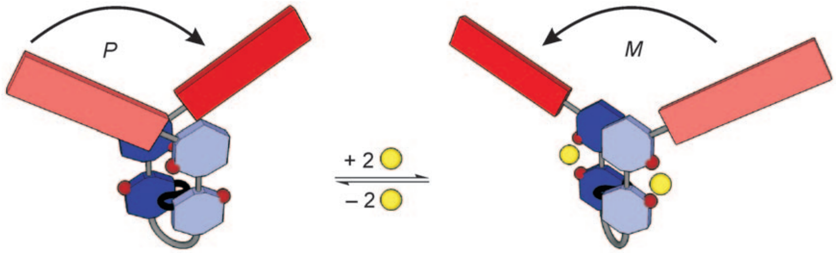
Carbene or not carbene? By utilizing [Cp$_2$Ti(η^2-Me$_3$SiC$_2$SiMe$_3$)] (Cp = C$_5$H$_5$) as both a reducing and a quenching agent in the reaction with R–N=C=N–R, the first paramagnetic dinuclear titanocene(III) carbene-like complex is prepared in good yield. The complex features the topology of a four-membered N-heterocyclic carbene species but with a Ti^{III} center as part of the heterocycle.



Molecular Machines

G. Haberhauer* ________ 9286–9289

A Metal-Ion-Driven Supramolecular Chirality Pendulum



Tick tock: The arms of a chirality pendulum can be completely and reversibly moved forward and backward like the pendulum of a clock by coordination and removal of a metal center (see picture). Each motion leads to a complete inversion of the configuration (swinging forth: *P*→*M* and swinging back: *M*→*P*).

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).

Service

Spotlight on Angewandte's Sister Journals ________ ***9032–9034***

Keywords ________ ***9290***

Authors ________ ***9291***

Preview ________ ***9293***