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

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama, H. Tokuyama**
Total Synthesis of (+)-Haplophytine

G. A. Zelada, J. Riu, A. Düzgün, F. X. Rius**
Immediate Detection of Living Bacteria at Ultra-Low Concentrations Using a Carbon-Nanotube-Based Potentiometric Aptasensor

*K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama**
Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

A. Giannis, P. Heretsch, V. Sarli, A. Stößel*
Synthesis of Cyclopamine Using a Biomimetic and Diastereoselective Approach

*W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski**
***tert*-Butyl End-Capped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*D. C. K. Rathwell, S.-H. Yang, K. Y. Tsang, M. A. Brimble**
An Efficient Formal Synthesis of the Human Telomerase Inhibitor (±)-γ-Rubromycin

C. A. Strassert, M. Otter, R. Q. Albuquerque, A. Höne, Y. Vida, B. Maier, L. De Cola**
Photoactive Hybrid Nanomaterial for Targeting, Labeling, and Killing Antibiotic Resistant Bacteria

Author Profile

"If I could be anyone for a day, I would be Barack Obama. The secret of being a successful scientist is dedication, integrity and hard work. …"
This and more about Timothy J. Donohoe can be found on page 7121.

Books

Highlights

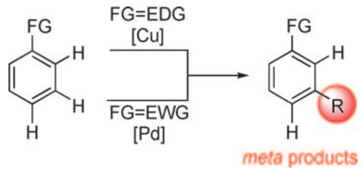
Asymmetric Catalysis

The best of both worlds: A combination of organocatalysis and transition-metal catalysis serve in the highly stereoselective and atom-economical reductive amination of a broad range of ketones. A chiral Brønsted acid catalyst facilitates the formation of protonated imines in situ and serves as chiral counteranion, while a chiral iridium complex catalyzes the reduction with elemental hydrogen.

C—H Activation

Y. Zhou, J. Zhao,* L. Liu* — **7126 – 7128**

Meta-Selective Transition-Metal Catalyzed Arene C—H Bond Functionalization



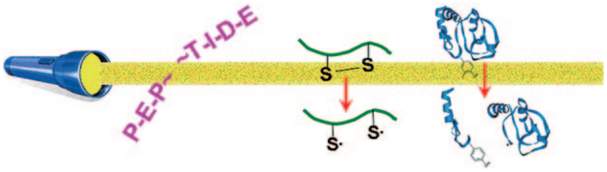
The selectivity is meta! Recent developments on transition-metal catalyzed *meta*-selective C—H functionalization are highlighted (see scheme; EDG = electron-donating group, EWG = electron-withdrawing group). The method is complementary to traditional methodologies and might provide numerous opportunities to access previously difficult organic products. Possible mechanisms are discussed.

Minireviews

Mass Spectrometry

T. Ly, R. R. Julian* ——— **7130 – 7137**

Ultraviolet Photodissociation: Developments towards Applications for Mass-Spectrometry-Based Proteomics



Shedding light on proteomics: The chemical diversity found in proteins presents a tremendous challenge for proteome analysis. Recent developments in ultraviolet photodissociation mass spectrometry (see illustration of selective fragmentation in a protein) have provided promising analytical tools for proteomics, particularly with respect to selective fragmentation, de novo sequencing, and the identification of posttranslational modifications.

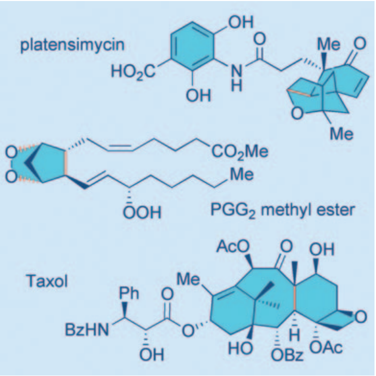
Reviews

Samarium Diiodide

K. C. Nicolaou,* S. P. Ellery, J. S. Chen ——— **7140 – 7165**

Samarium Diiodide Mediated Reactions in Total Synthesis

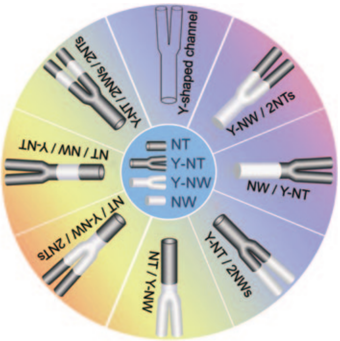
A powerful and versatile single-electron reductant that has found extensive use in the synthesis of complex molecules such as those shown in the scheme (Bz = benzoyl, PGG_2 = prostaglandin G_2) is samarium diiodide (SmI_2). Representative examples illustrate its scope and versatility, with special emphasis on cascade sequences.



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*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (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.

Communications

A large variety of interconnected nanowire/nanotube (NW/NT) and nanotube/nanowire/nanotube (NT/NW/NT, see picture) hybrid architectures with branched topology have been prepared using a combinatorial process of electrodepositing nanowires in the branched channels of anodic aluminum oxide templates, selectively etching part of the deposited nanowires, and growing nanotubes in the remaining empty channels on the ends of the nanowires.



Nanoarchitectures

G. W. Meng,* F. M. Han, X. L. Zhao,
B. S. Chen, D. C. Yang, J. X. Liu, Q. L. Xu,
M. G. Kong, X. G. Zhu, Y. J. Jung,
Y. J. Yang, Z. Q. Chu, M. Ye, S. Kar,
R. Vajtai, P. M. Ajayan ______ **7166 – 7170**

A General Synthetic Approach to Interconnected Nanowire/Nanotube and Nanotube/Nanowire/Nanotube Heterojunctions with Branched Topology

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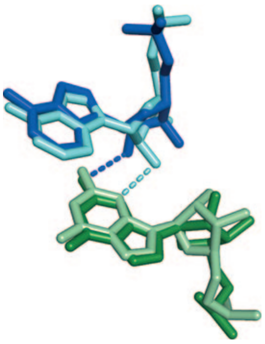

Enzymes establish intricate networks of interactions to catalyze reactions, and X-ray crystallography is a powerful tool for the visualization of such networks. But what happens when different structural models (see picture) suggest different interactions for the same residue? Functional data based on double-mutant cycles can provide an answer, as shown for the *Tetrahymena* group I ribozyme.

RNA Catalysis

M. Forconi, R. N. Sengupta, M.-C. Liu,
A. C. Sartorelli, J. A. Piccirilli,*
D. Herschlag* ____________ **7171 – 7175**

Structure and Function Converge To Identify a Hydrogen Bond in a Group I Ribozyme Active Site

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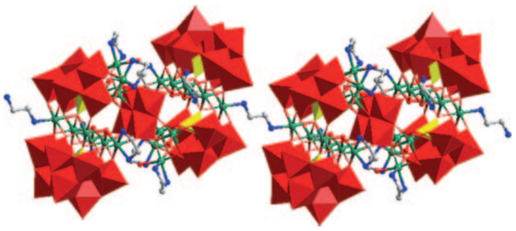
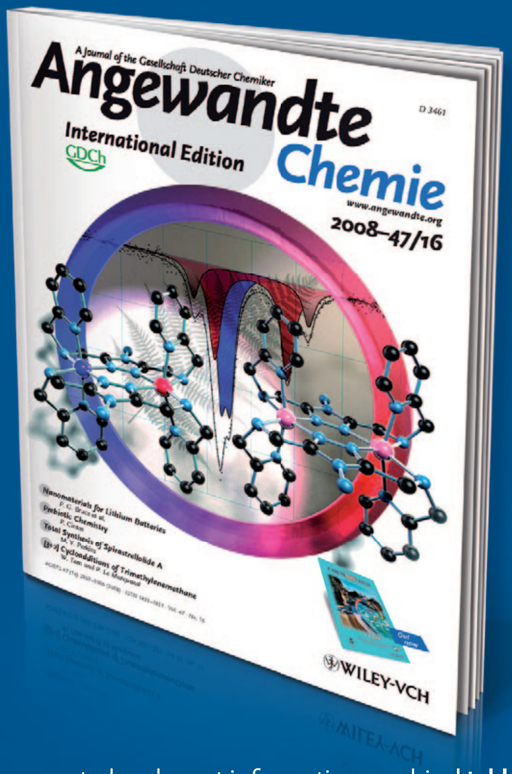


Line them up: Under hydrothermal conditions, trilacunary Keggin {B-α-PW_9O_{34}} fragments and nickel ions form the two largest Ni-substituted poly(polyoxotungstate)s with the greatest number of Ni ions in a known polyoxometalate. Bridging amine ligands connect the fragments to form the 1D structure of the polyoxometalates (see structure; red octahedra WO_6, yellow tetrahedra PO_4, green Ni, red O, blue N, gray C).

Poly(polyoxometalate)s

S.-T. Zheng, J. Zhang,
J. M. Clemente-Juan,* D.-Q. Yuan,
G.-Y. Yang* ______________ **7176 – 7179**

Poly(polyoxotungstate)s with 20 Nickel Centers: From Nanoclusters to One-Dimensional Chains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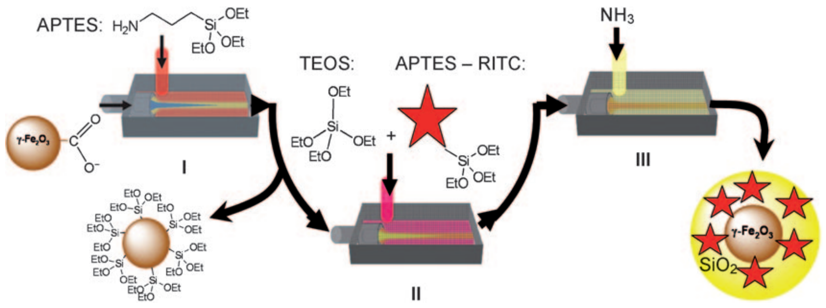
Microreactor Networks

A. Abou-Hassan,* R. Bazzi, V. Cabuil ______ 7180 – 7183

Multistep Continuous-Flow Microsynthesis of Magnetic and Fluorescent γ-Fe_2O_3@SiO_2 Core/Shell Nanoparticles

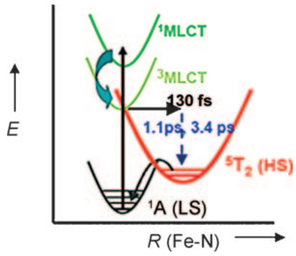


Coupled microreactors allow fast, continuous, multistep synthesis of the title compound. Thus, grafting with APTES is carried out in microreactor I, mixing with sol–gel TEOS and APTES labeled with Rhodamine B isothiocyanate (RITC) in II, and coating in III. This technique opens the way to developing a lab-on-a-chip platform for nanoparticle synthesis.

Vibrational Dynamics

C. Consani, M. Prémont-Schwarz, A. ElNahhas, C. Bressler, F. van Mourik, A. Cannizzo, M. Chergui* __ 7184 – 7187

Vibrational Coherences and Relaxation in the High-Spin State of Aqueous $[Fe^{II}(bpy)_3]^{2+}$



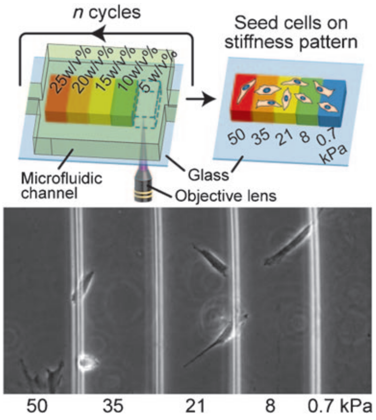
Dizzy cooling: Femtosecond excitation of the singlet states of aqueous $[Fe^{II}(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) leads to the formation of a vibrationally hot quintet state that exhibits wave-packet dynamics arising from a chelate-ring and bending mode. The vibrational relaxation involves at least two modes: the Fe–N stretching mode (see picture) and the coherently excited chelate-ring and bending mode, which relax on different time scales.

Micropatterning

Y. K. Cheung, E. U. Azeloglu, D. A. Shiovitz, K. D. Costa, D. Seliktar, S. K. Sia* ______ 7188 – 7192

Microscale Control of Stiffness in a Cell-Adhesive Substrate Using Microfluidics-Based Lithography

Microfluidics-based lithography based on microfluidics is used to pattern cell-adhesive hydrogel substrates with microvariations in stiffness. The micropatterns are generated by feeding PEG-fibrinogen and various amounts of polyethylene glycol diacrylate (PEGDA) into the micofluidic channel (see picture).

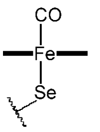


Cytochrome P450

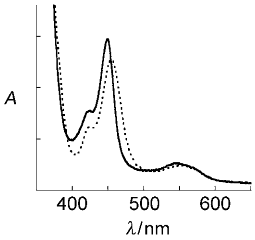
Y. Jiang, S. Sivaramakrishnan, T. Hayashi, S. Cohen, P. Moënne-Loccoz, S. Shaik, P. R. Ortiz de Montellano* _ 7193 – 7195

Calculated and Experimental Spin State of Seleno Cytochrome P450

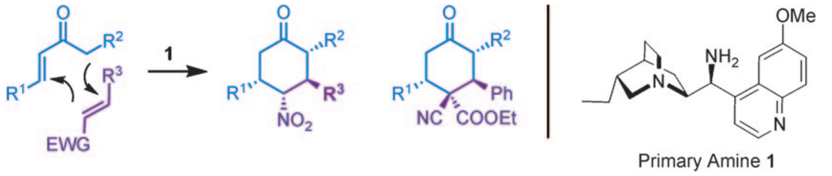
A change for the better: The proximal cysteine thiolate in a cytochrome P450 enzyme is replaced by a selenocysteine. The resulting selenolate-ligated CYP119 protein has UV/Vis (see spectrum, •••••), EPR, and resonance Raman spectra that are similar to those of the native protein (——). These results are the first to fully describe a hemoprotein with a selenolate proximal ligand.



SeCYP119

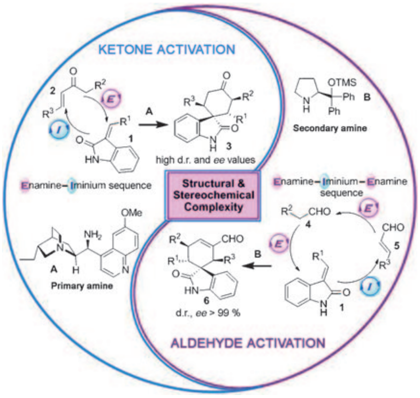


Asymmetric Organocatalysis



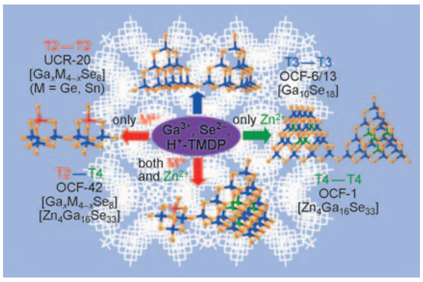
Primary amines do it differently: Acyclic α,β-unsaturated ketones are activated toward a characteristic stepwise double-Michael addition sequence by chiral primary amine catalysis, which offers a powerful alternative in the design of synthetically useful organocascade reactions (see scheme, EWG = electron-withdrawing group). This method complements the Diels–Alder reaction for the one-step synthesis of complex cyclohexane scaffolds with excellent optical purity.

Synthetic Methods



Not so complex: The asymmetric one-step construction of multiple stereocenters in complex spirocyclic oxindoles was achieved with very high fidelity by using distinct organocascade reactions utilizing two organocatalysts, each activating different carbonyl compounds (see scheme; TMS = trimethylsilyl). The complementary approaches demonstrate the potential of organocascade catalysis to face challenging synthetic problems.

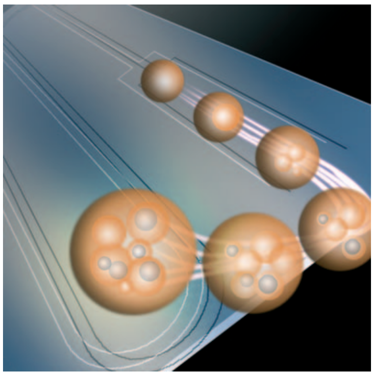
Solid-State Structures



Controlling the charge: 3D open-framework selenide superlattices based on T2 and T4 supertetrahedral clusters were synthesized using charge-complementary and geometry-matching metal cations such as Zn^{2+}/Ga^{3+}/Ge^{4+}. The clusters are joined into the covalent superlattices with an unequal ratio of 1:4, leading to a framework topology that can be simplified into a previously unknown tetrahedral net.

Multiple Emulsions

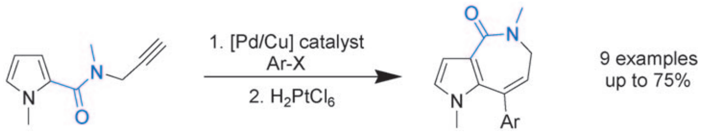
Transforming emulsions: A straightforward method for turning a single emulsion into multiple emulsions in a common T-junction microfluidic device has been achieved. Water is introduced into oil using a cosolvent; a single emulsion then forms at a T junction, which is followed by the autocatalytic formation of a multiple emulsion by cosolvent shifting into the continuous phase.



Catalytic Cycloisomerization

M. Gruit, D. Michalik, A. Tillack, M. Beller* ———— **7212 – 7216**

Platinum-Catalyzed Intramolecular Cyclizations of Alkynes: Efficient Synthesis of Pyrroloazepinone Derivatives

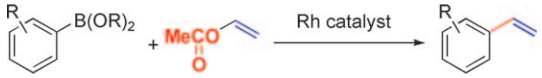


Achieving closure: A platinum-catalyzed cycloisomerization reaction (see scheme; $[Pd/Cu] = [PdCl_2(PPh_3)_2]/CuI$, Ar = aryl, X = Br,I) is used for the efficient straightforward synthesis of biologically relevant pyrrolo-[3,2-*c*]azepin-4-one derivatives.

Cross-Coupling

J.-Y. Yu, R. Kuwano* ———— **7217 – 7220**

Rhodium-Catalyzed Cross-Coupling of Organoboron Compounds with Vinyl Acetate



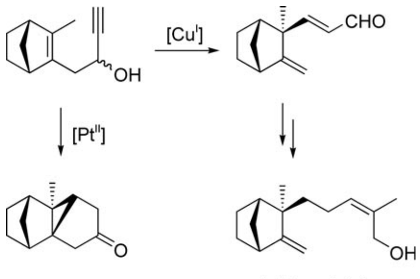
A new coupling partner: Vinyl acetate couples with organoboron compounds in the presence of a rhodium catalyst; carbon–carbon bond formation occurs on the vinylic carbon attached to the acetoxy group. Conventional nickel and palladium catalysts were found to be ineffective for the reaction.

Rearrangement Reactions

C. Fehr,* I. Magpantay, J. Arpagaus, X. Marquet, M. Vuagnoux ———— **7221 – 7223**

Enantioselective Synthesis of (−)-β-Santalol by a Copper-Catalyzed Enynol Cyclization–Fragmentation Reaction

The right cat for the desired odor: The key step in an enantioselective synthesis of the prized fragrance (−)-β-santalol was a highly selective copper-catalyzed cyclization–fragmentation reaction of an enynol (see scheme). When a platinum catalyst was used for the cyclization step, the desired fragmentation did not take place; instead, a product containing a cyclopropane ring was formed with 100% selectivity.

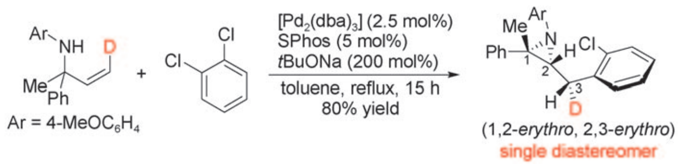


(−)-β-santalol

Synthetic Methods

S. Hayashi, H. Yorimitsu,* K. Oshima* ———— **7224 – 7226**

Synthesis of Aziridines by Palladium-Catalyzed Reactions of Allylamines with Aryl and Alkenyl Halides: Evidence of a *syn*-Carboamination Pathway



Crazy rings: Treatment of *N*-arylallylamine with an aryl or alkenyl halide under palladium catalysis (see scheme; dba = dibenzylideneacetone, SPhos = 2-dicyclohexylphosphanyl-2′,6′-dimethoxybiphenyl) resulted in intramolecular cyclization to form the arylmethyl-substituted aziridine with concomitant C–C bond formation. The experiments for the elucidation of the reaction mechanism are also described.

Reaction Mechanisms

W.-X. Zhang, S. Zhang, X. Sun, M. Nishiura, Z. Hou,* Z. Xi* ———— **7227 – 7231**

Zirconium- and Silicon-Containing Intermediates with Three Fused Rings in a Zirconocene-Mediated Intermolecular Coupling Reaction

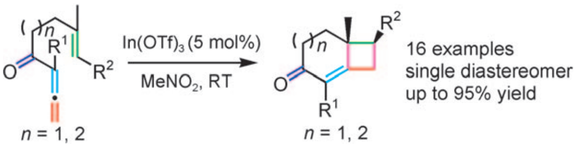
Veritable Jack-in-the-box: The isolation and characterization of key Zr/Si-containing intermediates was achieved for a zirconocene-mediated intermolecular coupling reaction (see scheme). The fate of the various functional groups was determined, and the reactivity of intermediate **1** with a variety of unsaturated substrates was also investigated.

Contents

Fused-Ring Systems

J. F. Zhao, T. P. Loh* ______ **7232 – 7235**

Acid-Catalyzed Intramolecular [2+2] Cycloaddition of Ene-allenones: Facile Access to Bicyclo[*n*.2.0] Frameworks

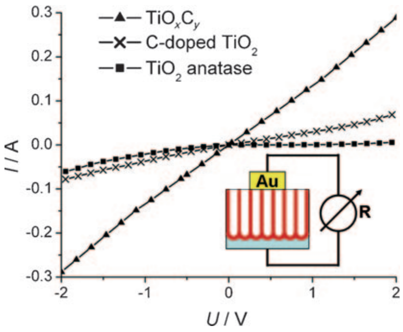


Two plus two equals a bicycle: A highly efficient acid-catalyzed intramolecular [2+2] cycloaddition of ene-allenones affords strained bicyclo[*n*.2.0] frameworks, which contain vicinal all-carbon quaternary and tertiary centers (see scheme; Tf: trifluoromethanesulfonyl), under mild conditions with excellent yields and chemo-, regio-, and diastereoselectivities.

Conductive TiO$_2$

R. Hahn, F. Schmidt-Stein, J. Salonen, S. Thiemann, Y. Y. Song, J. Kunze, V.-P. Lehto, P. Schmuki* ____ **7236 – 7239**

Semimetallic TiO$_2$ Nanotubes



Orchestrating conductors: A carbo-thermal reduction treatment of a TiO$_2$ nanotube layer in acetylene converts the tube walls into highly conductive and stable oxy carbide compounds. The resulting semimetallic TiO$_2$ nanotube layers (TiO$_x$C$_y$) are electrode materials with properties that differ from other TiO$_2$ nanotubes (see picture). They have a high oxygen overpotential and can be used as a catalyst support, for example, for methanol oxidation.

Biological Signaling

T. Knoth, K. Warburg, C. Katzka, A. Rai, A. Wolf, A. Brockmeyer, P. Janning, T. F. Reubold, S. Eschenburg, D. J. Manstein, K. Hübel, M. Kaiser, H. Waldmann* ______ **7240 – 7245**

The Ras Pathway Modulator Melophlin A Targets Dynamins

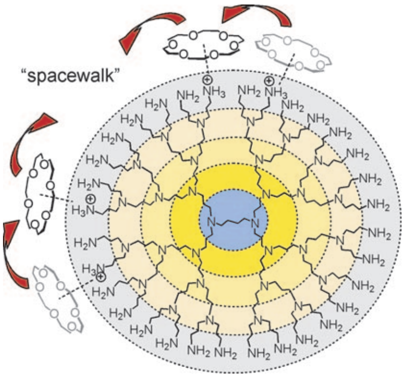
Natural causes: A combination of organic synthesis, chemical proteomics, biophysics, and cell and molecular biology investigations reveals that the natural product melophlin A (purple) influences signal propagation through the Ras network by interfering with the function of dynamins (green) in endocytosis.

Dendrimers

H. D. F. Winkler, D. P. Weimann, A. Springer, C. A. Schalley* _ **7246 – 7250**

Dynamic Motion in Crown Ether Dendrimer Complexes: A “Spacewalk” on the Molecular Scale

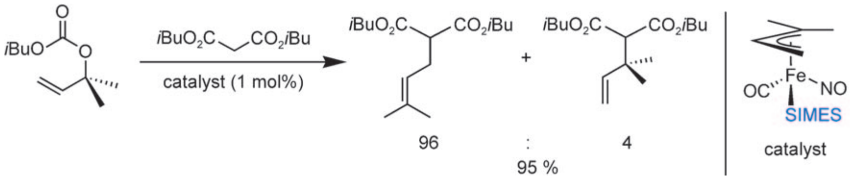
Walking on the edge: Mass spectrometry aided by H/D exchange experiments provides evidence for a surprisingly quick movement of [18]crown-6 units across the periphery of POMAM dendrimers (see picture). In the diluted gas phase, dissociation/reassociation equilibria do not play any role. The movement of the crown ether units resembles that of astronauts on the outside of a space station.



Allylic Substitutions

M. Holzwarth, A. Dieskau, M. Tabassam, B. Plietker* ______ **7251 – 7255**

Preformed π-Allyl Iron Complexes as Potent, Well-Defined Catalysts for the Allylic Substitution

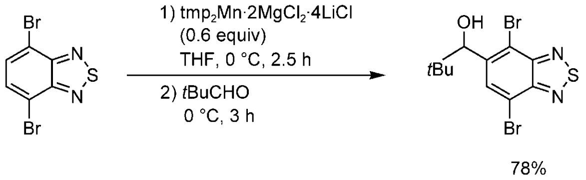


Reanimation: Catalytically inactive π-allyl iron complexes are “reanimated” upon addition of N-heterocyclic carbene ligands such as 1,3-dimesitylimidazolin-2-ylidene (SIMES). A comparison of stoichiometric and catalytic allylic alkylation reactions shows the π-allyl mechanism to be active in this catalytic system.

Directed Manganation

S. H. Wunderlich, M. Kienle, P. Knochel* ______ **7256 – 7260**

Directed Manganation of Functionalized Arenes and Heterocycles Using $tmp_2Mn{\cdot}2\,MgCl_2{\cdot}4\,LiCl$



Convenient metalation procedures: Directed manganation using $tmp_2Mn{\cdot}2\,MgCl_2{\cdot}4\,LiCl$ leads to the corresponding diorganomanganese reagents in high yields at 0–25 °C. Remarkably, a number of functionalities as well as sensitive heterocycles are tolerated in this metalation procedure (see scheme). The organomanganese species react with a great variety of electrophiles and undergo efficient oxidative amination reactions.

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