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:

*A. Asati, S. Santra, C. Kaittanis, S. Nath, J M. Perez**
Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles

*J.-Q. Wang, S. Stegmaier, T. F. Fässler**
$[Co@Ge_{10}]^{3-}$: An Intermetalloid Cluster with an Archimedean Pentagonal Prismatic Structure

L. Xu, C. E. Doubleday, K. N. Houk**
Dynamics of 1,3-Dipolar Cycloadditions of Diazonium Betaines with Acetylene and Ethylene: Bending Vibrations Facilitate Reaction

*C. Chandler, P. Galzerano, A. Michrowska, B. List**
The Proline-Catalyzed Double Mannich Reaction of Acetaldehyde with *N*-Boc imines

*P. Antoni, Y. Hed, A. Nordberg, D. Nyström, H. von Holst, A. Hult, M. Malkoch**
Bifunctional Dendrimers: From Robust Synthesis and Accelerated One-Pot Postfunctionalization Strategy to Potential Applications

*M. S. Nikolic, C. Olsson, A. Salcher, A. Kornowski, A. Rank, R. Schubert, A. Frömsdorf, H. Weller, S. Förster**
Micelle and Vesicle Formation of Amphiphilic Nanoparticles

*R. M. van der Veen, C. J. Milne, A. El Nahhas, F. A.Lima, V.-T. Pham, J. Best, J. A. Weinstein, C. N. Borca, R. Abela, C. Bressler, M. Chergui**
Structural Determination of a Photochemically Active Diplatinum Molecule by Time-Resolved EXAFS Spectroscopy

*G. Seidel, R. Mynott, A. Fürstner**
Elementary Steps of Gold Catalysis: NMR Spectroscopy Reveals the Highly Cationic Character of a Gold Carbenoid

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-walled Carbon Nanotube

News


J. S. Johnson


M. J. Gaunt


R. Berger

Author Profile

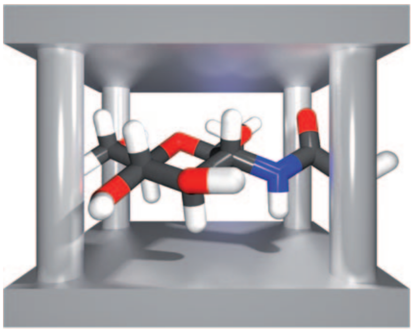
“I chose chemistry as a career because… I like the creative challenge. My favorite subjects at school were mathematics and music…!” These facts and more information about Alan E. Rowan can be found on page 1717

Books

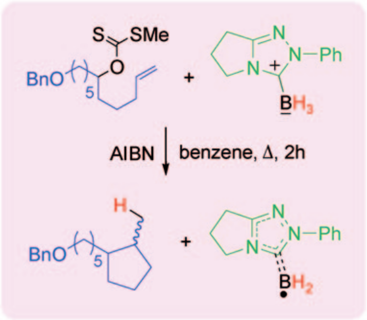
Highlights

Carbohydrates

Improving on Mother Nature? The carbohydrate recognition demonstrated by supramolecular systems in water can now compete with that of natural systems, both in terms of affinity and selectivity. A synthetic carbohydrate receptor displays similar affinity for *N*-acetyl-D-glucosamine derivatives as the lectin wheat germ agglutinin and even greater selectivity (see picture: gray C, white H, blue N, red O).

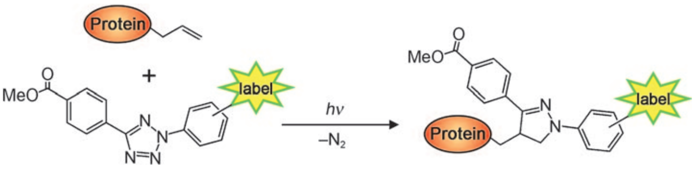


Radical Reduction



Undue influence: N-heterocyclic carbenes (NHCs) were found to reduce the strength of the B–H bonds of borane by a surprisingly large amount upon the formation of NHC–BH_3 complexes. This property was exploited in the development of a suite of NHC–borane complexes for the reduction of xanthates in radical-mediated Barton–McCombie-type deoxygenation reactions (see scheme). AIBN = azobisisobutyronitrile, Bn = benzyl.

Protein Modification



The light-induced formation of a covalent bond between an alkene group and a tetrazole moiety has been used for the selective labeling of proteins in vitro and in live cells. This bioorthogonal ligation initiated by brief irradiation with UV light leads to a fluorescent pyrazoline adduct (see scheme).

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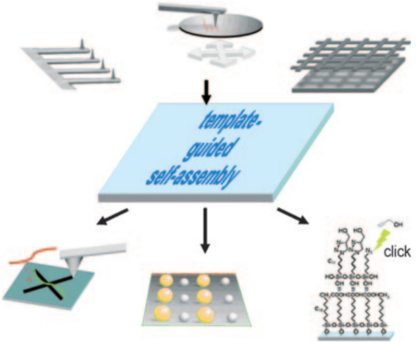
Minireviews

Surface Patterning

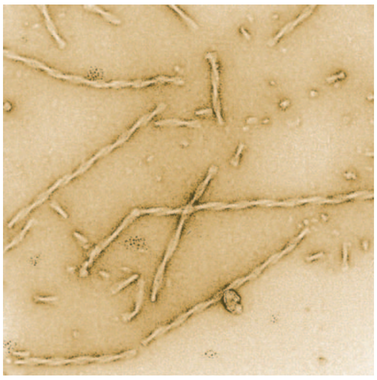
Surfaces with purposes: The electroinitiated patterning of self-assembled monolayers enables the fabrication of a variety of complex nanostructures (see picture). The possibilities offered by the introduction of chemical selectivity through the local generation of chemically active groups and subsequent derivatization are reviewed, with a focus on progress in this area of research over the last four years.



Reviews

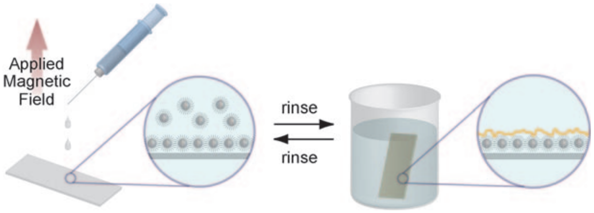
Medicinal Chemistry

Small molecules against Alzheimer's: The pathological aggregation of the tau protein is a major hallmark of neurodegenerative diseases such as Alzheimer's disease. The inhibition or reversal of tau aggregation is a potential therapeutic strategy that is currently undergoing clinical trials. The image shows pathological fibers assembled from tau protein, which are the main components of the neurofibrillary tangles of Alzheimer's disease.



Communications

Ultrathin Films



Getting organized: Assemblies of ferromagnetic FePt nanoparticles were generated with large perpendicular magnetic anisotropy by a magnetic-field-assisted layer-by-layer method, and subsequently layer-by-layer films consisting of $L1_0$-FePt nanoparticles and organic polymers were prepared. These films are phototunable when photochromic molecules are used as polymer layers.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Ionic Liquids
High-Throughput MicroRNA Profiling
Macroscopic Chirality
NMR Spectroscopy
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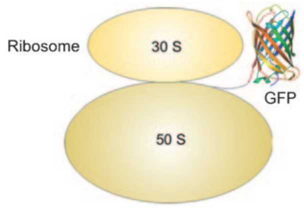
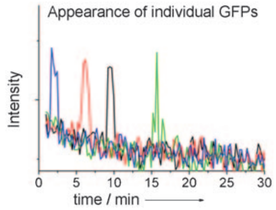
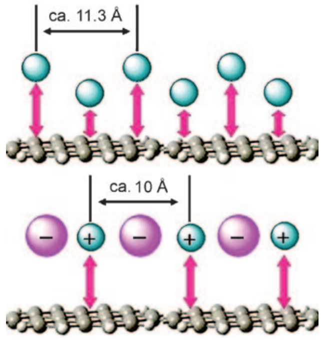
Protein Folding





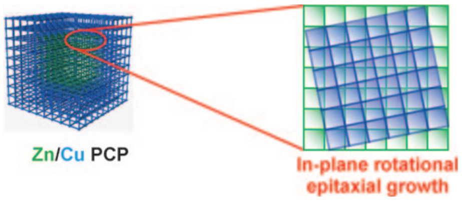
It's not easy being green: Real-time visualization of labeled ribosomes and de novo synthesized green fluorescent protein molecules using single-molecule-sensitive fluorescence microscopy demonstrates that the mutant GFPem is produced with a characteristic time of five minutes. Fluorescence of the fastest GFP molecules appears within one minute (see picture).

Surface Structures



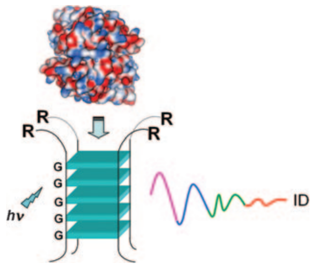
Complex patterns: The arene manganese tricarbonyl complexes [Mn(η^5-2,5-didodecoxy-1,4-semiquinone)$(CO)_3$] and [Mn(η^6-1,4-dioctyloxybenzene)$(CO)_3$]BF_4 form patterned monolayers on the surface of highly ordered pyrolytic graphite (HOPG), as a result of hydrogen-bonding, hydrophobic, and electrostatic interactions, leading to an ordered 2D array of manganese atoms or ions.

Metal–Organic Frameworks



MOF on MOF: Core–shell porous coordination polymer (PCP) crystals are fabricated at the single-crystal level by epitaxial growth in solution. Synchrotron X-ray diffraction measurements unveiled the structural relationship between the shell crystal and the core crystal, where in-plane rotational epitaxial growth compensates the difference in lattice constant.

Sensors



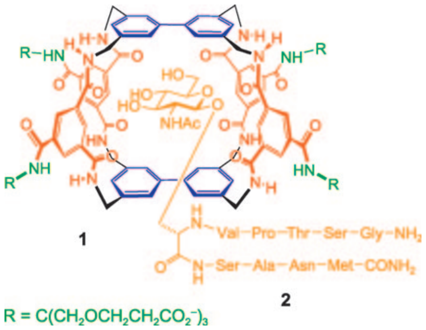
Sniffing out proteins: Fluorescent DNA G-quadruplexes have been used for building versatile signaling receptors for proteins in a single solution. Introducing a protein sample to the ensemble results in a unique emission signature for unambiguous identification (see scheme, R = fluorophore). The self-assembled, pattern-based protein detection systems are easily fabricated, have the potential for high-throughput operations, and have the ability to handle small protein samples.

Carbohydrate Recognition

Y. Ferrand, E. Klein, N. P. Barwell,
M. P. Crump, J. Jiménez-Barbero,
C. Vicent, G.-J. Boons, S. Ingale,
A. P. Davis* ______ 1775 – 1779

A Synthetic Lectin for O-Linked β-*N*-Acetylglucosamine

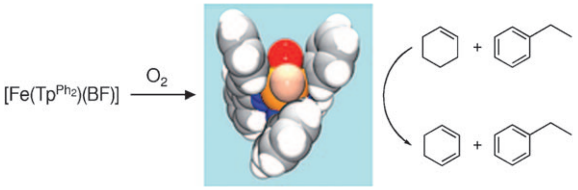
Changing employment: Receptor **1** binds β-*N*-acetylglucosaminyl (β-GlcNAc) up to 100 times more strongly than it does glucose. This synthetic lectin shows affinities similar to wheat germ agglutinin (WGA), a natural lectin used to bind GlcNAc. Remarkably, **1** is more selective than WGA. It favors especially the glycoside unit in glycopeptide **2**, a model of the serine-*O*-GlcNAc posttranslational protein modification.



Shape-Selective Oxidation

A. Mukherjee, M. Martinho,
E. L. Bominaar, E. Münck,*
L. Que, Jr.* ______ 1780 – 1783

Shape-Selective Interception by Hydrocarbons of the O_2-Derived Oxidant of a Biomimetic Nonheme Iron Complex

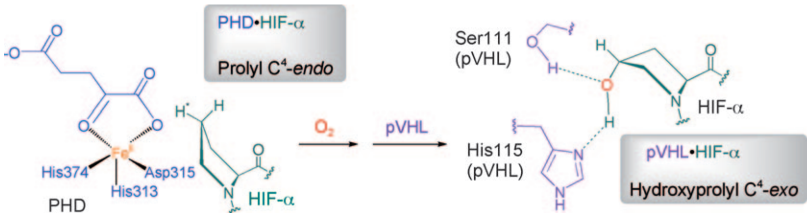


Picky ferryl: The complex $[Fe(Tp^{Ph_2})(BF)]$ (Tp^{Ph_2} = hydrotris(3,5-diphenylpyrazolyl)-borate; BF = benzoylformate) reacts with O_2 to generate an oxidant (see picture; O red, pink; Fe yellow; N blue; C gray; H white) that oxidizes added hydrocarbons shape-selectively. Discrimination derives from a cleft formed by two phenyl groups of the Tp^{Ph_2} ligand, favoring oblate spheroidal substrates.

Conformational Analysis

C. Loenarz, J. Mecinović, R. Chowdhury,
L. A. McNeill, E. Flashman,
C. J. Schofield* ______ 1784 – 1787

Evidence for a Stereoelectronic Effect in Human Oxygen Sensing



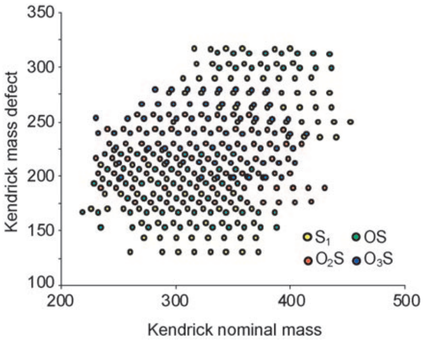
How PHDs achieve specificity: *trans*-4-prolyl hydroxylation of the transcription factor HIF occurs with stereochemical retention. Substrate-analogue studies show how the von Hippel Lindau tumor suppressor protein (pVHL) and the oxygen-sensing hydroxylases (PHDs) achieve specificity for hydroxyprolyl/prolyl residues for the C^4-*exo*/*endo* prolyl conformations, respectively.

Crude Oil Analysis

S. K. Panda, J. T. Andersson,
W. Schrader* ______ 1788 – 1791

Characterization of Supercomplex Crude Oil Mixtures: What Is Really in There?

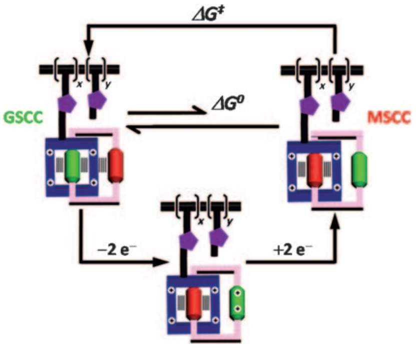
Through different windows: One major obstacle in energy research is the complexity and variety of compounds present in crude oil. A study of different ionization methods for mass spectrometry shows that the mass spectrum very strongly depends on which method is used.



Molecular Electronics

M. A. Olson, A. B. Braunschweig, L. Fang, T. Ikeda, R. Klajn, A. Trabolsi, P. J. Wesson, D. Benítez, C. A. Mirkin, B. A. Grzybowski,* J. F. Stoddart* —— **1792 – 1797**

A Bistable Poly[2]catenane Forms Nanosuperstructures

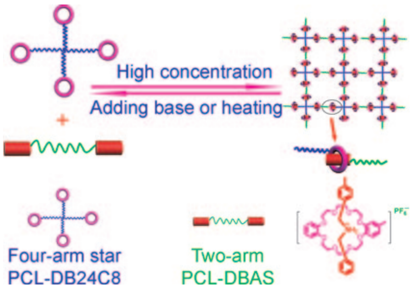


Side-chain poly[2]catenanes at the click of a switch! A bistable side-chain poly[2]catenane has been synthesized and found to form hierarchical self-assembled hollow superstructures of nanoscale dimensions in solution. Molecular electromechanical switching (see picture) of the material is demonstrated, and the ground-state equilibrium thermodynamics and switching kinetics are examined as the initial steps towards processible molecular-based electronic devices and nanoelectromechanical systems.

Supramolecular Gels

Z. Ge, J. Hu, F. Huang,* S. Liu* —— **1798 – 1802**

Responsive Supramolecular Gels Constructed by Crown Ether Based Molecular Recognition

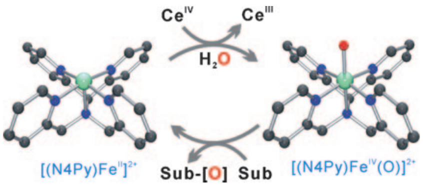


Responsive supramolecular gels were constructed from crown ether terminated four-arm star poly(ε-caprolactone) (PCL–DB24C8) and dibenzylammonium-terminated two-arm PCL–DBAS (see scheme), exploiting the formation of pseudorotaxane linkages between crown ether and ammonium moieties. The resultant supramolecular gels exhibit thermo- and pH-induced reversible gel–sol transition.

Enzyme Models

Y.-M. Lee, S. N. Dhuri, S. C. Sawant, J. Cho, M. Kubo, T. Ogura, S. Fukuzumi,* W. Nam* —— **1803 – 1806**

Water as an Oxygen Source in the Generation of Mononuclear Nonheme Iron(IV) Oxo Complexes

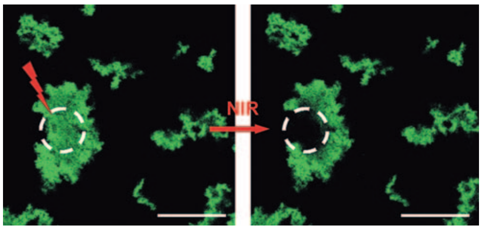


Give me an “O”! Mononuclear nonheme iron(IV) oxo complexes have been generated using water as an oxygen source and cerium(IV) as an oxidant. The high-yield oxygenation of organic substrates in this system (see picture, Fe green, O red, N blue, C gray) is catalyzed by iron(II) complexes. The source of oxygen in the iron(IV) oxo complexes and the oxygenated products has been assigned unambiguously by isotopic labeling experiments.

Vesicle-Based Drug Delivery

D. V. Volodkin,* A. G. Skirtach,* H. Möhwald —— **1807 – 1809**

Near-IR Remote Release from Assemblies of Liposomes and Nanoparticles

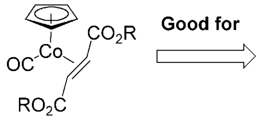


Set free by light: Near-IR (NIR) laser-initiated remote release of fluorescent dye from complexes of liposome–gold-nanoparticle aggregates is demonstrated (see fluorescence images). Complexes of the desired size are shown to be a viable approach to the construction of vesicle-based drug-delivery systems with light-triggered remote release characteristics. This opens up a new method to manipulate liposome-based drug-delivery systems in a biocompatible way by using the near-IR spectral range.

Cycloaddition Catalysts

A. Geny, N. Agenet, L. Iannazzo,
M. Malacria, C. Aubert,*
V. Gandon* ______ **1810 – 1813**

Air-Stable $\{(C_5H_5)Co\}$ Catalysts for [2+2+2] Cycloadditions

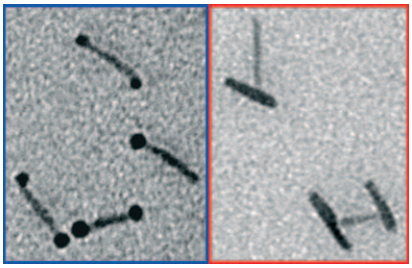


Cobalt cyclopentadienyl complexes incorporating a fumarate and a CO ligand (see picture) efficiently catalyze inter- and intramolecular [2+2+2] cycloadditions of alkynes, nitriles, and/or alkenes to give benzenes, pyridines, or 1,3-cyclohexadienes. Unlike catalysts such as $[CpCo(CO)_2]$ or $[CpCo(C_2H_4)_2]$ $(Cp = C_5H_5)$, they are air-stable, easy to handle, compatible with microwave conditions, and do not necessarily require irradiation to be active.

Nanostructures

J. Maynadié, A. Salant, A. Falqui,
M. Respaud, E. Shaviv, U. Banin,
K. Soulantica,* B. Chaudret **1814 – 1817**

Cobalt Growth on the Tips of CdSe Nanorods

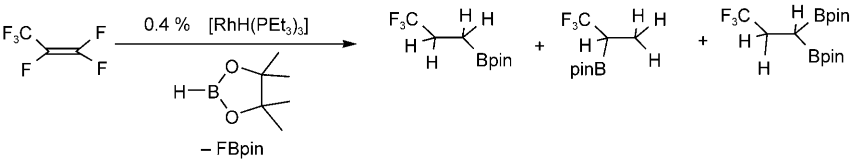


Best of both worlds: Reduction of an organometallic Co precursor on preformed CdSe nanorods yields two distinct semiconducting–magnetic heterostructures (see picture). The selective growth of Co on the tips of CdSe first gives nanosphere–nanorod dimers, which evolve into nanorod–nanorod structures. In the hybrid objects the magnetic properties of Co remain intact, while the luminescence properties of CdSe are affected but not completely quenched.

Catalytic C–F Activation

T. Braun,* M. Ahijado Salomon,
K. Altenhöner, M. Teltewskoi,
S. Hinze ______ **1818 – 1822**

C–F Activation at Rhodium Boryl Complexes: Formation of 2-Fluoroalkyl-1,3,2-Dioxaborolanes by Catalytic Functionalization of Hexafluoropropene



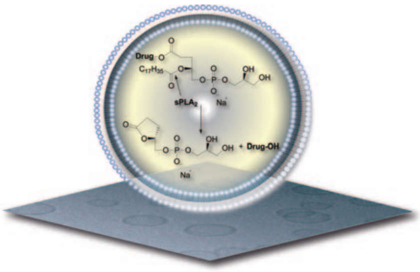
Fluorinated building blocks by C–F bond cleavage: Catalytic C–F activation reactions that give novel dioxaborolanes have been developed (see scheme). The reactions proceed at room temperature, and catalytic intermediates are presumably rhodium hydride and boryl species.

Medicinal Chemistry

L. Linderoth, G. H. Peters, R. Madsen,
T. L. Andresen* ______ **1823 – 1826**

Drug Delivery by an Enzyme-Mediated Cyclization of a Lipid Prodrug with Unique Bilayer-Formation Properties

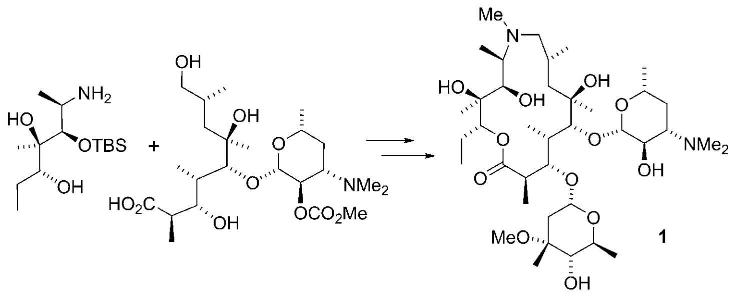
Special delivery: Liposomal drug-delivery systems in which prodrugs are activated specifically by disease-associated enzymes have great potential for the treatment of severe diseases, such as cancer. A new type of phospholipid-based prodrug has the ability to form stable small unilamellar vesicles (see picture). Activation of the prodrug vesicles by the enzyme $sPLA_2$ initiates a cyclization reaction, which leads to the release of the drug.



Natural Products

H. C. Kim, S. H. Kang* ——— **1827 – 1829**

Total Synthesis of Azithromycin

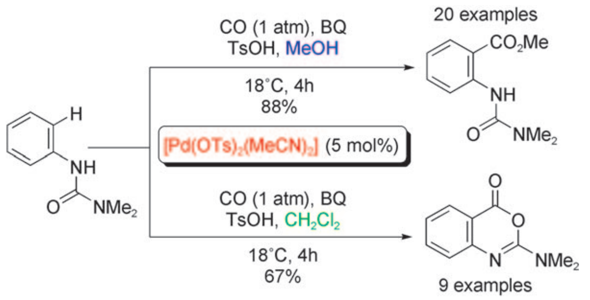


The quaternary king: Azithromycin (**1**), which has improved pharmacological profiles compared with erythromycins, was the target of an enantioselective synthesis. All the stereogenic quaternary carbon centers were elaborated by a desymmetrization of 2-substituted glycerols using a chiral imine/$CuCl_2$ catalyst.

C–H Activation

C. E. Houlden, M. Hutchby, C. D. Bailey, J. G. Ford, S. N. G. Tyler, M. R. Gagné, G. C. Lloyd-Jones,* K. I. Booker-Milburn* ——— **1830 – 1833**

Room-Temperature Palladium-Catalyzed C–H Activation: *ortho*-Carbonylation of Aniline Derivatives

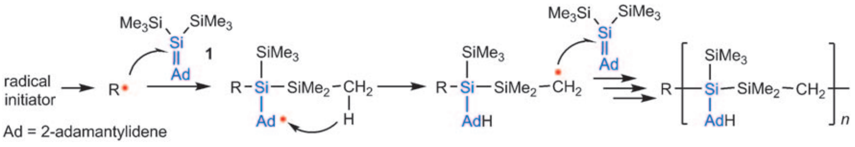


Pd and CO—ureally got me! The title reaction proceeds efficiently at 18 °C under CO (1 atm) with 5 % $[Pd(OTs)_2(MeCN)_2]$ as precatalyst. Depending on the solvents used, either anthranilates or cyclic imides can be obtained in high yields (see picture, BQ = benzoquinone, Ts = 4-toluenesulfonyl).

Polycarbosilanes

D. Bravo-Zhivotovskii,* S. Melamed, V. Molev, N. Sigal, B. Tumanskii, M. Botoshansky, G. Molev, Y. Apeloig* ——— **1834 – 1837**

Radical Polymerization of the Silene $(Me_3Si)_2Si{=}CR_2$ by Hydrogen Transfer from a Trimethylsilyl Group

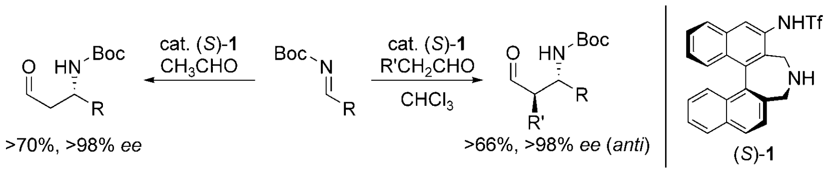


The silene $(Me_3Si)_2Si{=}Ad$ is polymerized to produce a polycarbosilane with an unusual Si–Si–C repeating backbone, rather than the Si–C or Si–Si–C–C units expected for olefinic radical polymerization. The polymer structure and the polymerization mechanism (see scheme) were studied by GPC, EPR, and NMR spectroscopy and by trapping experiments.

Organocatalysis

T. Kano, Y. Yamaguchi, K. Maruoka* ——— **1838 – 1840**

A Designer Axially Chiral Amino Sulfonamide as an Efficient Organocatalyst for Direct Asymmetric Mannich Reactions of N-Boc-Protected Imines

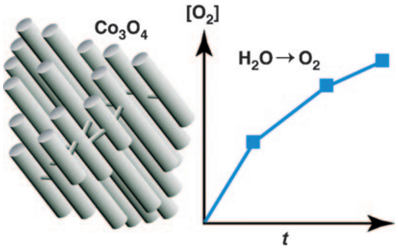


The moderate nucleophilicity of the axially chiral amino sulfonamide (*S*)-**1** suppresses the problematic side reactions, including aldol reactions, in the asymmetric Mannich reaction of N-Boc-protected imines with aldehydes. The corresponding adducts are obtained in good yield and excellent stereoselectivity (see scheme; Boc = *tert*-butoxycarbonyl, Tf = trifluoromethanesulfonyl).

Water Oxidation

F. Jiao, H. Frei* ______ **1841 – 1844**

Nanostructured Cobalt Oxide Clusters in Mesoporous Silica as Efficient Oxygen-Evolving Catalysts

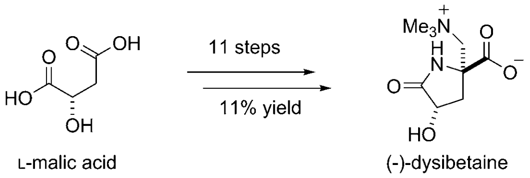


Light, inexpensive, effective: Nanostructured Co_3O_4 clusters (see picture) in mesoporous silica are the first example of a nanometer-sized multielectron catalyst made of a first-row transition-metal oxide that evolves oxygen from water efficiently. The nanorod bundle structure of the catalyst results in a very large surface area, an important factor contributing to the high turnover frequency.

Natural Product Synthesis

J. Isaacson, Y. Kobayashi* __ **1845 – 1848**

An Ugi Reaction in the Total Synthesis of (−)-Dysibetaine

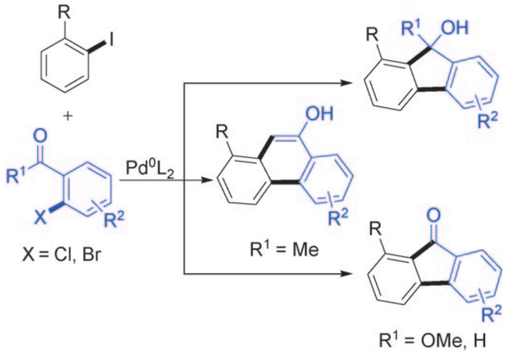


(−)-Dysibetaine has been synthesized in 11 steps from readily available L-malic acid (see scheme). The key step is a unique Ugi 4-center-3-component cyclization reaction, where an ester group acts as the carboxylic acid component. The use of 1,1,1,3,3,3-hexamethyldisilazane as an ammonia equivalent and a specially designed isocyanide leads to an expeditious synthesis.

Domino Reactions

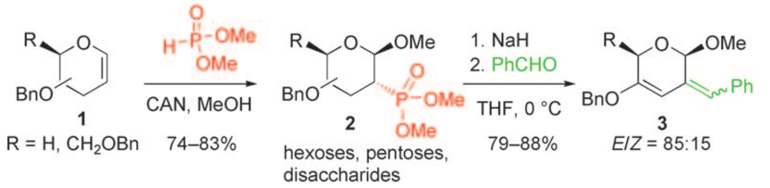
Y.-B. Zhao, B. Mariampillai, D. A. Candito, B. Laleu, M. Li, M. Lautens* **1849 – 1852**

Exploiting the Divergent Reactivity of Aryl–Palladium Intermediates for the Rapid Assembly of Fluorene and Phenanthrene Derivatives



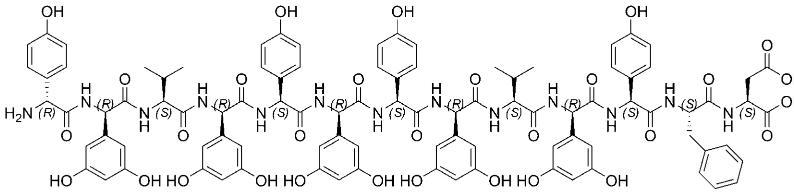
They all fall down: The value of domino processes can be greatly enhanced when the possibility exists for one to selectively diverge from a common intermediate. In preliminary studies the dual reactivity of aryl–palladium intermediates is exploited. A diverse array of fluorene and phenanthrene derivatives were synthesized in a rapid and efficient manner (see scheme).

Carbohydrate Analogues



Phosphorus meets carbohydrates: Dimethyl phosphite reacts with ceric(IV) ammonium nitrate (CAN) to give phosphonyl radicals that add to glycals **1**. The derivatives **2** were isolated in high yields and during a subsequent Horner–Emmons reaction underwent an interesting elimination to give 3,6-dihydro-2*H*-pyrans **3**. The short sequence with simple precursors is applicable to the transformation of hexoses, pentoses, and disaccharides. Bn = benzyl.

Natural Products Synthesis


1

An adaptable approach: The first highly convergent stereoselective synthesis of feglymycin (see structure) and its enantiomer is based on the coupling of repeating peptide fragments. The use of weakly basic conditions throughout the synthesis suppressed the epimerization of sensitive aryl glycine units. Feglymycin has strong anti-HIV activity as well as potent (previously identified as weak) antibacterial activity against *Staphylococcus aureus*.

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

Corrigendum

Highly Efficient and Thermally Stable Organic Sensitizers for Solvent-Free Dye-Sensitized Solar Cells

H. Choi, C. Baik, S. O. Kang, J. Ko,*
M.-S. Kang, Md. K. Nazeeruddin,*
M. Grätzel ______________ **327–330**

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In this Communication, the following phrase has to be included in the first paragraph of the experimental section on page 330:
"The photocurrents were measured with an AM 1.5 simulator (1000 W Oriel Solar Simulators No. 92199A) using a NREL-certified silicon diode for calibration but without correction for spectral mismatch between the silicon cell and the DSSC."