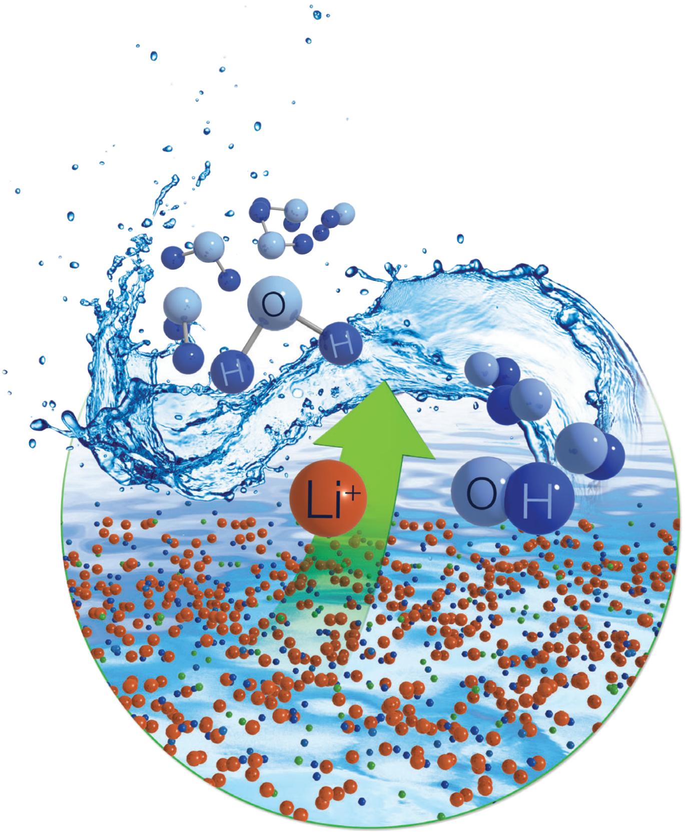
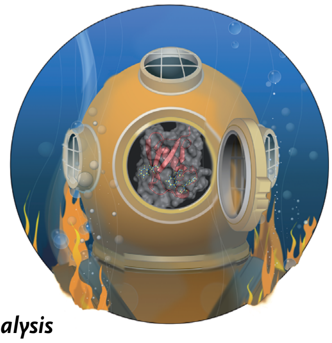
Superstable Separators ...

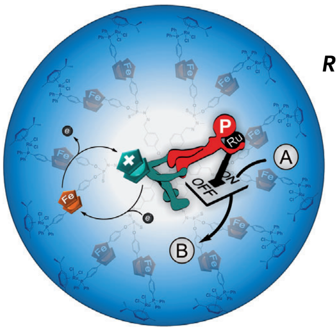


… (solid electrolytes) are required for novel aqueous-based high-energy lithium batteries, to enable their long-term operation. In their Communication on page 129 ff., C. Ma, M. Chi, et al. demonstrate excellent stability and conductivity of the cubic $Li_7La_3Zr_2O_{12}$ garnet in neutral and strongly basic solutions, indicating it may be the ideal solid electrolyte for next-generation high-energy lithium batteries.

Conformational Analysis

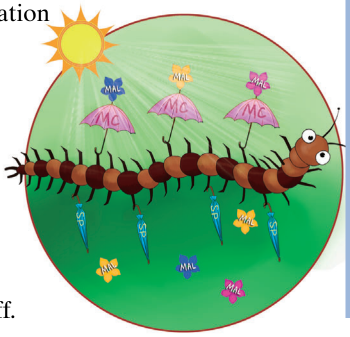
In their Communication on page 102 ff., A. J. Wand et al. investigated the aromatic side chains of ubiquitin, which show a sharp thermal dynamical transition at approximately 312 K.





Redox-Switchable Catalysis

The development of a ferrocenylphosphane ruthenium(II) catalyst that can be reversibly switched off and on through chemical oxidation and reduction is described by E. Hey-Hawkins et al. in their Communication on page 311 ff.



Thiol Click Reaction

The reversible photoactivated thiol formation of spirothiopyran confers spatiotemporal sequential control to a thiol click reaction, as described by L. Zhu et al. in their Communication on page 174 ff.

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Editorial

Miscellaneous

Author Profile

News

J. K. Nørskov

F. Diederich

F. Schüth

Obituaries

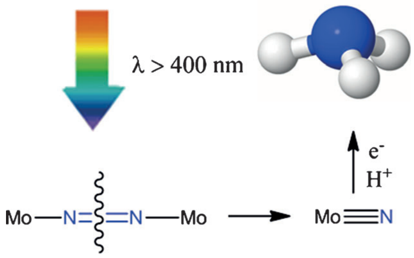
Ekkehard Winterfeldt, who was President of the Gesellschaft Deutscher Chemiker (German Chemical Society; GDCh) from 1996–1997 passed away on October 11, 2014. His research achievements included the synthesis of alkaloids and steroids, and stereoselective transformations. He was known as a gentleman and an inspiring scholar, and was able to convey his passion for science to everybody who worked with him.

Books

Highlights

Nitrogen Fixation

The split up: Recent advances in photochemical dinitrogen splitting have been achieved. Demonstration of the reversibility of the N_2 splitting and ammonia formation from a nitride has advanced the field of N_2 fixation using a synthetic homogeneous system.



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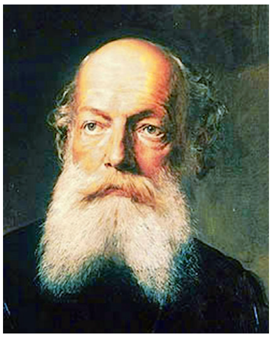
Essays

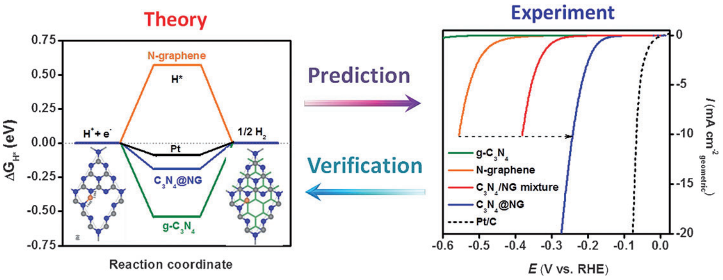
History of Science



In January 1865, August Kekulé (see picture) published his theory of the structure of benzene, which he later reported had come to him in a daydream about a snake biting its tail. Although other theories had been postulated before 1865, Kekulé was the first to identify the correct structure. Kekulé's theory resulted in a clear understanding of aromatic compounds and thus had a major impact on the development of chemical science and industry.

Minireviews

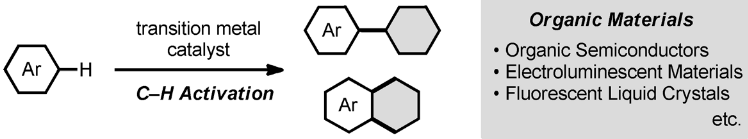
Hydrogen-Evolution Reaction



All for HER: A large number of high-performance electrocatalysts for the hydrogen-evolution reaction (HER) have been developed. Computational chemistry can direct the molecular design of these catalysts, and electrochemical experiments can be used to verify theoretical predictions.

Reviews

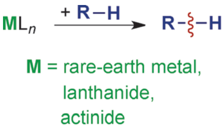
C–H Activation



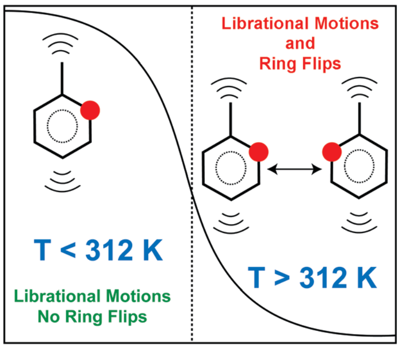
By no means π in the sky! The activation of aromatic C–H bonds by a transition metal catalyst has received significant attention in the synthetic chemistry community. In recent years, rapid and site-selective extension of π-electron systems by C–H activation has emerged as an ideal methodology for preparing conjugated organic materials. This Review focuses on recent developments in this area directed toward new optoelectronic materials.

C–H Activation

Potential of transition metals: Numerous known lanthanide and actinide complexes are able to selectively activate C–H bonds of organic substrates. However, the challenge of establishing a closed catalytic cycle still remains. Many f-block complexes show great potential in this important area of chemistry.



Communications

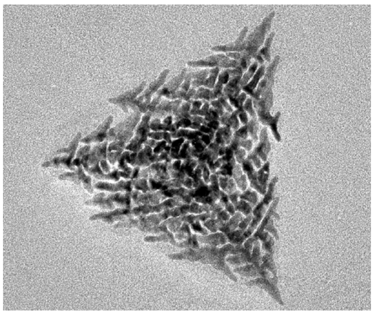


NMR relaxation methods revealed that the three aromatic side chains in human ubiquitin show a sharp thermal dynamical transition at approximately 312 K. Below the transition temperature, ring motion is largely librational whereas above this temperature, a complete ring-rotation process that is fully consistent with continuous diffusion not requiring the transient creation of a large activated free volume occurs.

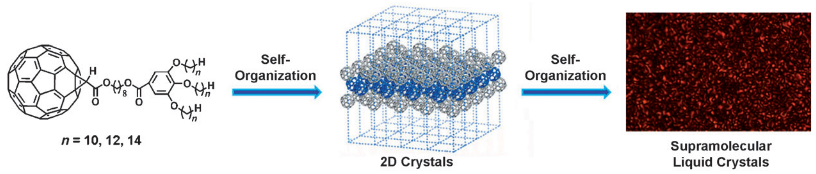
Conformational Analysis

Frontispiece

Hierarchical trigonal bipyramid nanoframes consisting of a Pt–Cu alloy with different Pt/Cu ratios are generated. Their size can be controlled in the range of 110–250 nm by varying the amount of KI in the reaction. In comparison to commercial Pt/C, these systems exhibit enhanced electrocatalytic activity in the oxidation of formic acid.



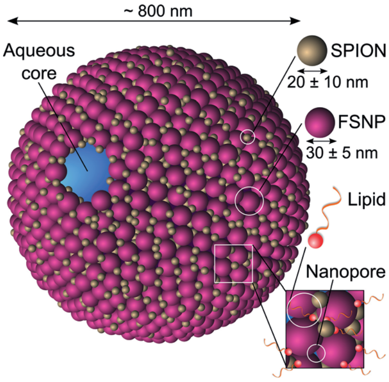
Formic Acid Oxidation



Soft materials: A series of fullerene dyads self-organize to form two-dimensional crystals through π–π interactions between fullerenes. Lamellar packing of the 2D crystals gives rise to the formation of a new family of thermotropic supramolecular liquid crystals with hierarchical structures.

Liquid Crystals

Outwardly functional but empty inside: Bifunctional submicron colloidosomes (see picture) were coassembled from superparamagnetic iron oxide nanoparticles (SPIONs) and fluorescent-dye-doped silica nanoparticles (FSNPs) at the interface between water-in-oil-emulsion droplets and then transferred by centrifugation to a fresh aqueous phase. These inherently rigid microcapsules feature a nanoporous shell and an aqueous core for active-agent encapsulation.

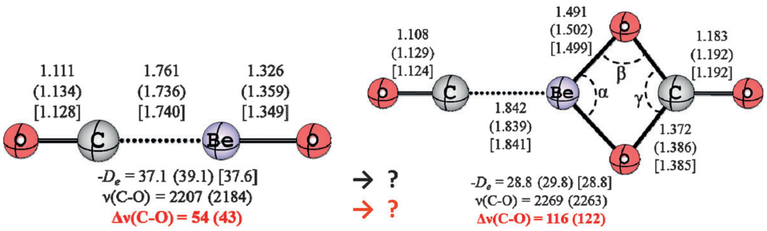


Microcapsules

Bonding Analysis

M. Chen, Q. Zhang, M. Zhou,*
D. M. Andrada, G. Frenking* **124 – 128**

Carbon Monoxide Bonding With BeO and $BeCO_3$: Surprisingly High CO Stretching Frequency of $OCBeCO_3$



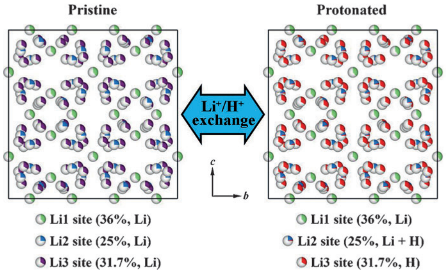
The carbonyl complex OC→$BeCO_3$ has been isolated in a neon matrix. The C–O stretching frequency exhibits a very strong blueshift with respect to free CO that is much higher than in OC→BeO although the donor–acceptor bond is significantly weaker. This is explained with the help of a quantum chemical bonding analysis, which also rationalizes the redshifts of the isomers OC→$BeCO_3$ and OC→BeO.

Lithium Batteries

C. Ma,* E. Rangasamy, C. Liang,
J. Sakamoto, K. L. More,
M. Chi* **129 – 133**

Excellent Stability of a Lithium-Ion-Conducting Solid Electrolyte upon Reversible Li^+/H^+ Exchange in Aqueous Solutions

Front Cover



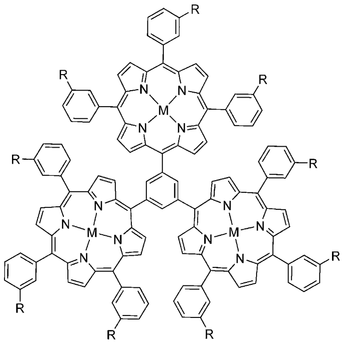
In sharp contrast to other garnets, the cubic $Li_7La_3Zr_2O_{12}$ preserved its structure upon Li^+/H^+ exchange in aqueous solutions. Subsequent immersion in a 2 M LiOH solution gave reverse Li^+/H^+ exchange, and the structure remained unchanged. Thus cubic $Li_7La_3Zr_2O_{12}$ has the desired properties to be the solid electrolyte in aqueous lithium batteries.

Homogeneous Catalysis

C. Maeda,* T. Taniguchi, K. Ogawa,
T. Ema* **134 – 138**

Bifunctional Catalysts Based on *m*-Phenylene-Bridged Porphyrin Dimer and Trimer Platforms: Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides

Metal matters: Triporphyrin catalysts $\mathbf{1}_{Mg}$ and $\mathbf{1}_{Zn}$ efficiently catalyzed the reaction of epoxides and CO_2 to form cyclic carbonates. The turnover number and turnover frequency reached 220000 and 46000 h^{-1}, respectively, for $\mathbf{1}_{Mg}$ and 310000 and 40000 h^{-1}, respectively, for $\mathbf{1}_{Zn}$, thus representing the highest values reported to date for this type of reaction.

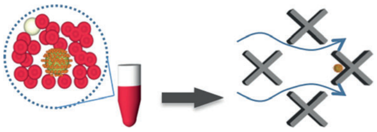


$\mathbf{1}_{Mg}$: M = Mg R = $O(CH_2)_6N^+Bu_3Br^-$
$\mathbf{1}_{Zn}$: M= Zn

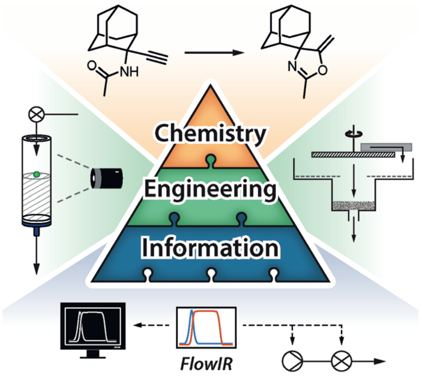
Cell Sorting

R. M. Mohamadi, J. D. Besant,
A. Mepham, B. Green, L. Mahmoudian,
T. Gibbs, I. Ivanov, A. Malvea, J. Stojcic,
A. L. Allan, L. E. Lowes, E. H. Sargent,
R. K. Nam, S. O. Kelley* **139 – 143**

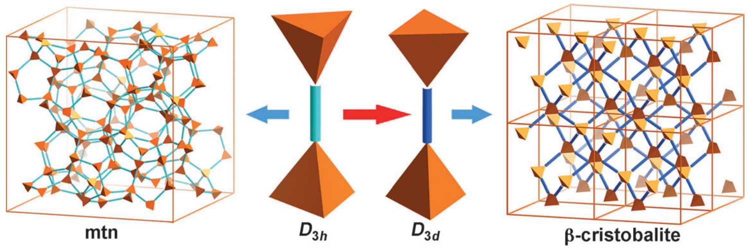
Nanoparticle-Mediated Binning and Profiling of Heterogeneous Circulating Tumor Cell Subpopulations



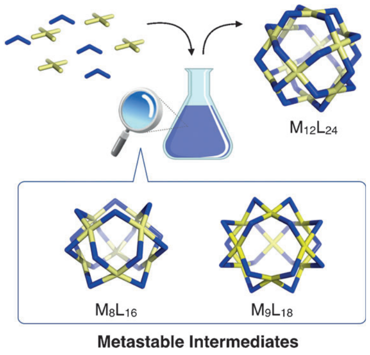
Separating subpopulations of cancer cells: Circulating tumor cells (CTCs) are inherently heterogeneous, and subpopulations may exist with varying clinical significance. A new device reads out differential levels of magnetic nanoparticle binding to profile subpopulations of CTCs with varying levels of surface expression, and provides a means to profile the epithelial-to-mesenchymal transition in patient CTCs.



Smart control: A new conceptual framework for the integration of multiple flow chemistry operations and downstream processing methods is described. Real-time data sharing between devices enables the construction of complex benchtop machine-assisted synthesis platforms. The concept is applied to the synthesis of 2-aminoadamantane-2-carboxylic acid, incorporating three chemistry steps and three workup steps into a single system.



Topological rationalization is used to design a zeotype mesoporous Zr metal–organic framework. When tetrahedra (orange; see picture) with $[M_3O(COO)_6]$ nodes and tridentate benzene-1,3,5-tricarboxylate faces are connected in an eclipsed configuration (D_{3h} nodes; light-blue bar), an mtn network is formed. A 60° rotation between tetrahedra gives a staggered configuration with D_{3d}-connected nodes (dark-blue bar) and a β-cristobalite network.



Geometrically dictated: Due to the geometrically restricted number of possible structures, the intermediates of self-assembly are rather relatively ordered than a chaotic mixture of numerous species. Two prominent metastable intermediates, M_8L_{16} and M_9L_{18}, are well characterized during the self-assembly of an $M_{12}L_{24}$ cuboctahedral complex.

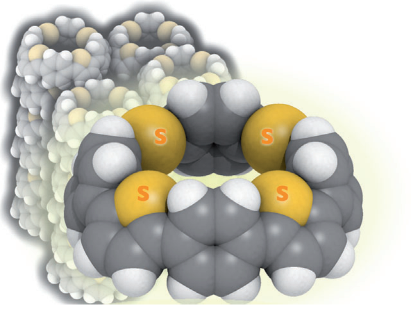
Macrocycles

H. Ito, Y. Mitamura, Y. Segawa,
K. Itami* ______ 159 – 163

Thiophene-Based, Radial π-Conjugation: Synthesis, Structure, and Photophysical Properties of Cyclo-1,4-phenylene-2′,5′-thienylenes

Inside Cover

Full circle: Cyclo-1,4-phenylene-2′,5′-thienylenes (CPTs) have been synthesized as the first example of a thiophene-based, radially π-conjugated system. X-ray crystal structures, UV-vis absorption and emission spectra, and theoretical studies revealed the unique structural and photophysical properties of CPTs based on their radial, cyclic π-conjugation.

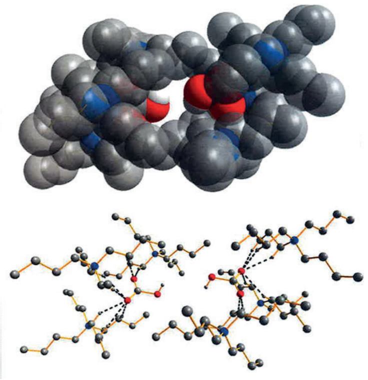


CO_2 Activation

S. L. Ackermann, D. J. Wolstenholme,* C. Frazee, G. Deslongchamps, S. H. M. Riley, A. Decken,
G. S. McGrady* ______ 164 – 168

Crystallographic Snapshot of an Arrested Intermediate in the Biomimetic Activation of CO_2

Capture the moment: In the molecule $[(n\text{-}C_4H_9)_4N]^+[HCO_3]^-$, the bulky arms of the cations give rise to a hydrophobic host scaffold (see picture) that emulates the substrate binding sites in carbonic anhydrase enzymes, affording a unique glimpse of an arrested intermediate in the base-mediated binding and activation of CO_2. $[(n\text{-}C_4H_9)_4N]^+[HCO_3]^-$ displays the longest C–O(H) bond detected in any uncoordinated hydrogencarbonate anion.

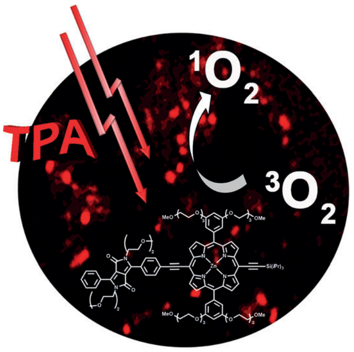


Photodynamic Therapy

J. Schmitt, V. Heitz,* A. Sour, F. Bolze,* H. Ftouni, J.-F. Nicoud, L. Flamigni,
B. Ventura* ______ 169 – 173

Diketopyrrolopyrrole-Porphyrin Conjugates with High Two-Photon Absorption and Singlet Oxygen Generation for Two-Photon Photodynamic Therapy

Excited! The title conjugates were prepared and characterized. They present high two-photon absorption (TPA) cross-sections as well as efficient singlet-oxygen generation, thus making them interesting sensitizers for two-photon excited photodynamic therapy.

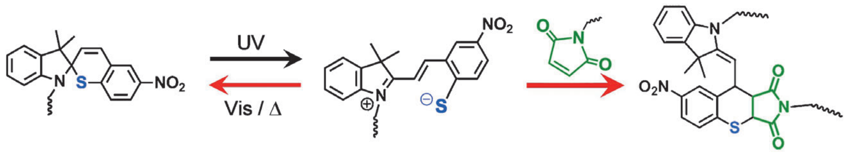


Photochemistry

Z. Liu, T. Liu, Q. Lin,* C. Bao,
L. Zhu* ______ 174 – 178

Sequential Control over Thiol Click Chemistry by a Reversibly Photoactivated Thiol Mechanism of Spirothiopyran

Back Cover

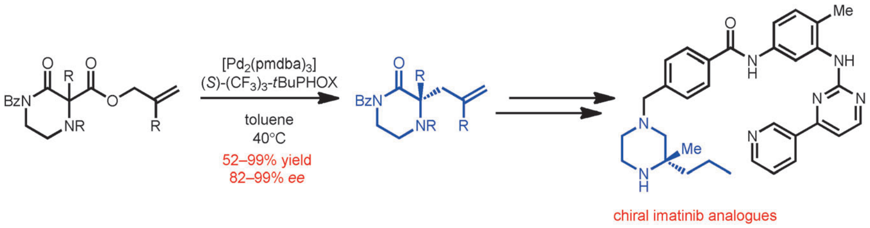


On demand: The reversible photoactivated thiol mechanism of spirothiopyran confers spatiotemporal sequential control on the thiol click reaction. Thus, a specific sequence of events can be easily attained by using just one type of thiol click photochemical reaction.

Asymmetric Catalysis

K. M. Korch, C. Eidamshaus,
D. C. Behenna, S. Nam, D. Horne,
B. M. Stoltz* ____ **179 – 183**

Enantioselective Synthesis of α-Secondary and α-Tertiary Piperazin-2-ones and Piperazines by Catalytic Asymmetric Allylic Alkylation



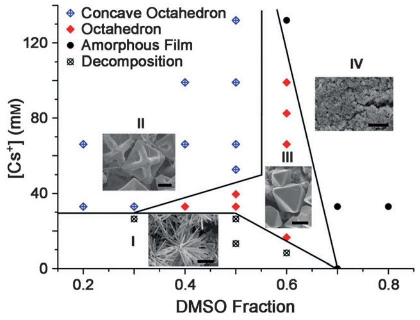
The 'pipe'line: The title reaction allows the synthesis of highly enantioenriched tertiary piperazine-2-ones. Deprotection and reduction affords the corresponding tertiary piperazines, which can be employed for the synthesis of medicinally important analogues including imatinib analogues. Bz = benzoyl, PHOX = phosphinooxazoline, pmdba = bis(*p*-methoxybenzylidene)acetone.

Supracrystals

Q. Yao, Y. Yu, X. Yuan, Y. Yu, D. Zhao,
J. Xie,* J. Y. Lee* ____ **184 – 189**

Counterion-Assisted Shaping of Nanocluster Supracrystals

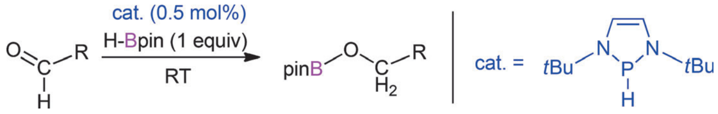
Nanocluster supracrystals: By replacing the H$^+$ counterions with Cs$^+$ ions, octahedral Ag$_{44}$ nanocluster supracrystals are obtained instead of the previously reported rhombohedra. The faces of the octahedral supracrystals can be further customized to be convex or concave simply by adjusting the Cs$^+$ concentration.



σ-Bond Metathesis

C.-C. Chong, H. Hirao,*
R. Kinjo* ____ **190 – 194**

Metal-Free σ-Bond Metathesis in 1,3,2-Diazaphospholene-Catalyzed Hydroboration of Carbonyl Compounds



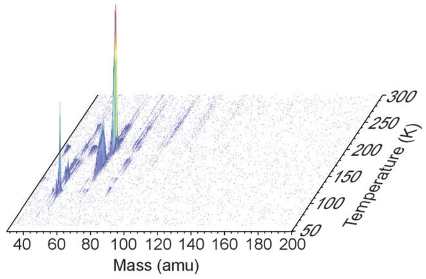
Leave the metal out: A catalytic amount of diazaphospholene effectively promotes a hydroboration reaction of various aldehydes and ketones under metal-free conditions. Kinetic and computational studies show that the reaction mechanism involves a σ-bond metathesis process occurring in a stepwise but nearly concerted manner.

Reaction Mechanism

R. I. Kaiser,* S. Maity,
B. M. Jones* ____ **195 – 200**

Synthesis of Prebiotic Glycerol in Interstellar Ices

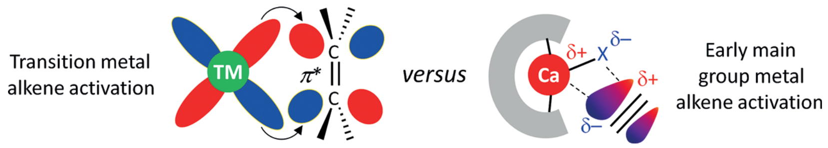
Icebreaker: Reported herein is the first in situ identification of glycerol, the key building block of all cellular membranes, formed by exposure of methanol-based interstellar model ices to ionizing radiation in the form of energetic electrons. These results provide compelling evidence that the radiation-induced formation of glycerol in low-temperature interstellar model ices is facile.



Hydroamination

J. Penafiel, L. Maron,
S. Harder* ______ 201–206

Early Main Group Metal Catalysis: How Important is the Metal?

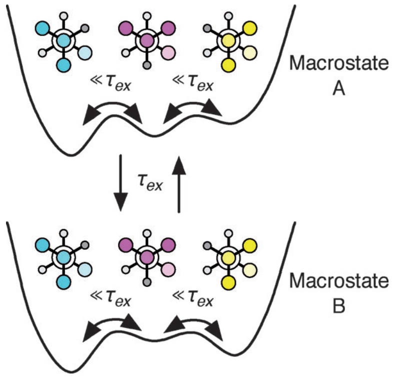


Organometallic catalysis or organocatalysis? Although alkene activation by transition metals is well-established, electrostatic activation by early main group metals is less effective. In some catalytic transformations the main group metal does not play a role, whereas in other processes the presence of a highly Lewis acidic metal is crucial.

Protein Dynamics

C. A. Smith, D. Ban, S. Pratihar, K. Giller, C. Schwiegk, B. L. de Groot, S. Becker, C. Griesinger,* D. Lee* ______ 207–210

Population Shuffling of Protein Conformations



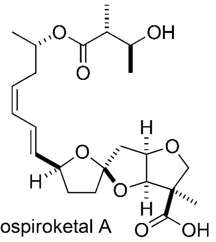
Connection of motions at different timescales: Slow motions alter the free energies, and thus populations, of protein side-chain conformations, which themselves interconvert on much faster timescales. The detection of these motions was enabled by advancements in relaxation dispersion experiments, that allow the measurement of motions as fast as 3.4 μs.

Natural Product Synthesis

S. Chang, S. Hur, R. Britton* ______ 211–214

Total Synthesis of Ascospiroketal A Through a Ag^I-Promoted Cyclization Cascade

Four candidate stereostructures of the marine octaketide ascospiroketal A were synthesized. The concise and highly stereocontrolled Ag^I-promoted cyclization cascade involves an oxetanyl ketochlorohydrin to access the entire tricyclic core of the natural product in one step. These syntheses also establish the full stereochemistry for the ascospiroketal natural products.

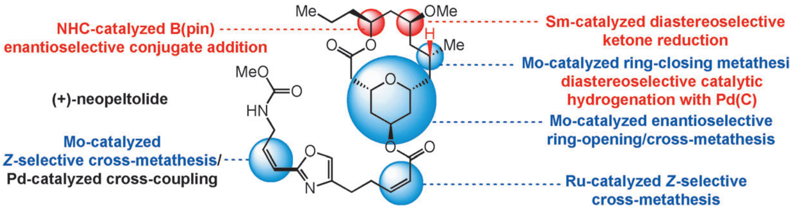


Ascospiroketal A

Olefin Metathesis

M. Yu, R. R. Schrock,
A. H. Hoveyda* ______ 215–220

Catalyst-Controlled Stereoselective Olefin Metathesis as a Principal Strategy in Multistep Synthesis Design: A Concise Route to (+)-Neopeltolide

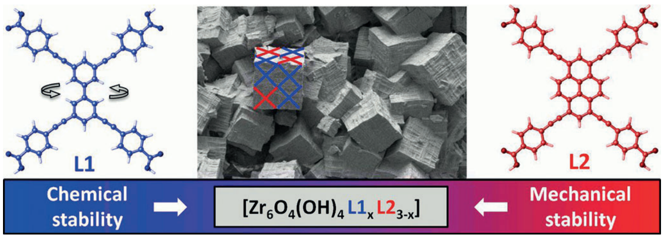


Powered by olefin metathesis: The antiproliferative agent neopeltolide has been prepared by a diastereo- and enantioselective route with a total of 28 steps and a longest linear sequence of 11 steps; catalytic processes were used to address every stereochemical issue. At the heart of the synthesis lie various selective Mo-, W-, or Ru-catalyzed metathesis reactions.

Metal–Organic Frameworks

S. B. Kalidindi, S. Nayak, M. E. Briggs,
S. Jansat, A. P. Katsoulidis, G. J. Miller,
J. E. Warren, D. Antypov, F. Corà, B. Slater,
M. R. Prestly, C. Martí-Gastaldo,
M. J. Rosseinsky* ———— **221 – 226**

Chemical and Structural Stability of Zirconium-based Metal–Organic Frameworks with Large Three-Dimensional Pores by Linker Engineering

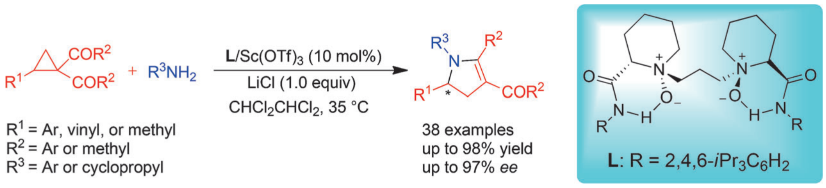


Two linkers of equivalent connectivity but quite distinct torsional flexibility are used to produce [Zr$_6$O$_4$(OH)$_4$(L1)$_{2.6}$(L2)$_{0.4}$]·(solvent)$_x$ that combines both structural and chemical stability in a metal–organic framework. Such a combination is not accessible for the single-linker isostructural phases. The resulting Zr-based MOF has three-dimensional channels and a high surface area of 4184 m^2 g^{-1}.

Asymmetric Catalysis

Y. Xia, X. H. Liu,* H. F. Zheng, L. L. Lin,
X. M. Feng* ———— **227 – 230**

Asymmetric Synthesis of 2,3-Dihydropyrroles by Ring-Opening/Cyclization of Cyclopropyl Ketones Using Primary Amines

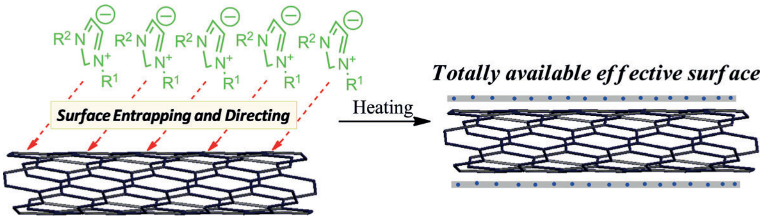


2,3-Dihydropyrroles are obtained in high yields and enantioselectivities through an enantioselective ring-opening/cyclization reaction of substituted cyclopropyl ketones with primary amine nucleophiles under mild reaction conditions. This method also provides an effective procedure for the kinetic resolution of 2-substituted cyclopropyl ketones.

Nanocarbon–Ionic Liquid Composites

Y. Ding, X. Sun, L. Zhang, S. Mao, Z. Xie,
Z. Liu, D. S. Su* ———— **231 – 235**

Entrapping an Ionic Liquid with Nanocarbon: The Formation of a Tailorable and Functional Surface

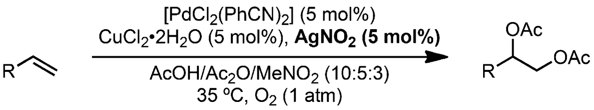


Utilizing the entrapping and directing effects of a nanocarbon graphitic surface, ionic liquids without cross-linkable groups, which were believed to be unable to be charred under pyrolysis conditions, could form a graphitic layer endowed with highly tailorable surface properties. B, N (blue dots), and C were confirmed to share same hexagonal rings, which provided more designable electronic properties.

Palladium Catalysis

Z. K. Wickens, P. E. Guzmán,
R. H. Grubbs* ———— **236 – 240**

Aerobic Palladium-Catalyzed Dioxygenation of Alkenes Enabled by Catalytic Nitrite

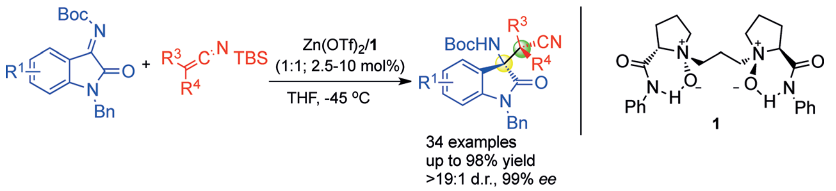


Catalytic amounts of nitrite were found to enable the carbon–oxygen bond-forming reductive elimination from unstable alkyl palladium intermediates. Dioxygenated products could be obtained from alkenes in high yields, employing molecular oxygen as the terminal oxidant. Insight into the C–O bond forming reductive elimination was obtained using ^{18}O-labeling experiments.

Homogeneous Catalysis

J. N. Zhao, B. Fang, W. W. Luo, X. Y. Hao, X. H. Liu, L. L. Lin, X. M. Feng* ________ 241 – 244

Enantioselective Construction of Vicinal Tetrasubstituted Stereocenters by the Mannich Reaction of Silyl Ketene Imines with Isatin-Derived Ketimines

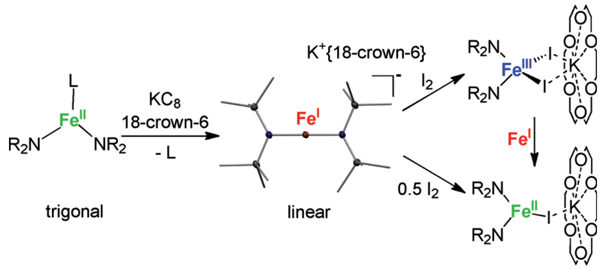


Getting crowded: The title reaction has been realized using a chiral *N*,*N*′-dioxide/Zn^{II} complex as the catalyst. A variety of β-amino nitriles containing congested vicinal tetrasubstituted stereocenters were obtained with excellent outcomes. A possible transition state has been proposed to explain the origin of the asymmetric induction. Boc = *tert*-butoxycarbonyl, TBS = *tert*-butyldimethylsilyl, Tf = trifluoromethanesulfonyl.

Low-Coordinate Metal Centers

C. G. Werncke, P. C. Bunting, C. Duhayon, J. R. Long, S. Bontemps,* S. Sabo-Etienne* ________ 245 – 248

Two-Coordinate Iron(I) Complex $[Fe\{N(SiMe_3)_2\}_2]^-$: Synthesis, Properties, and Redox Activity

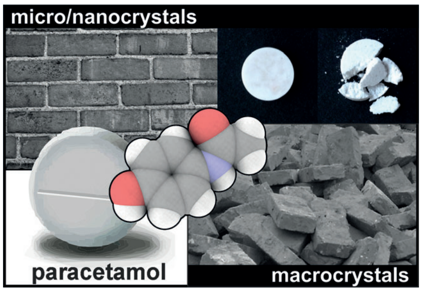


I, II, III, Iron: The linear two-coordinate iron(I) complex $[Fe\{N(SiMe_3)_2\}_2]^-$ is isolated in high yield through the reduction of either $[Fe\{N(SiMe_3)_2\}_2]$ or $[Fe\{N(SiMe_3)_2\}_2(PCy_3)]$. One- and two-electron oxidation by reaction with I_2 affords the corresponding iodo iron(II) and diiodo iron(III) complexes.

Sonocrystallization

D.-K. Bučar,* J. A. Elliott,* M. D. Eddleston, J. K. Cockcroft, W. Jones ________ 249 – 253

Sonocrystallization Yields Monoclinic Paracetamol with Significantly Improved Compaction Behavior

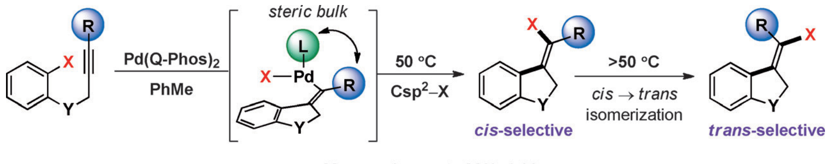


Compact discs: Experimental compaction and finite element analysis have shown that the poor compaction properties of paracetamol can be improved through sonocrystallization. The superior tabletability is attributed to the enhanced capacity of the solid to plastically deform and the increased cohesive interactions between its particles.

Carbohalogenation

C. M. Le, P. J. C. Menzies, D. A. Petrone, M. Lautens* ________ 254 – 257

Synergistic Steric Effects in the Development of a Palladium-Catalyzed Alkyne Carbohalogenation: Stereodivergent Synthesis of Vinyl Halides



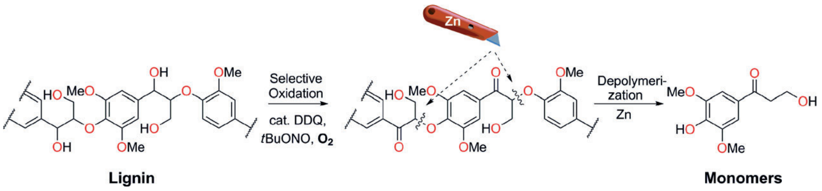
28 examples, up to 93% yield
up to >95:5 *cis*-selective, up to 9:1 *trans*-selective

Bulk makes it *E*–*Z*: By exploiting the synergistic steric effects between substrate and catalyst, an intramolecular Pd-catalyzed alkyne carbohalogenation can be realized. This reaction provides access to tetrasubstituted vinyl halides from the corresponding aryl halides.

Renewable Chemicals

C. S. Lancefield, O. S. Ojo, F. Tran,
N. J. Westwood* ________ 258 – 262

Isolation of Functionalized Phenolic Monomers through Selective Oxidation and C–O Bond Cleavage of the β-O-4 Linkages in Lignin

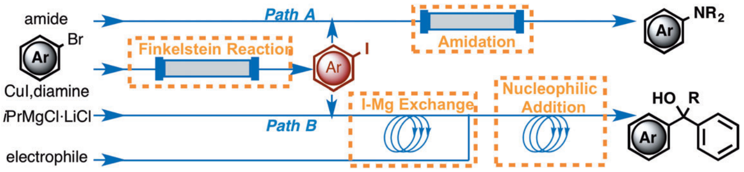


Lignin depolymerization: A two-step approach comprising the selective aerobic oxidation of the benzyl alcohols of lignin using DDQ/*t*BuONO/O_2 followed by cleavage of the β-O-4 linkages of lignin through treatment with metallic zinc affords functionalized small molecules. These products will be useful building blocks for the preparation of biomass-derived fine chemicals and materials.

Flow Chemistry

M. Chen, S. Ichikawa,
S. L. Buchwald* ________ 263 – 266

Rapid and Efficient Copper-Catalyzed Finkelstein Reaction of (Hetero)-Aromatics under Continuous-Flow Conditions

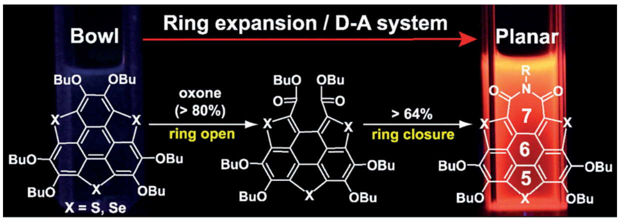


Synthesis in flow: A flow system has been developed that enables a rapid halogen exchange in the copper-catalyzed Finkelstein reaction of (hetero)aromatics. A broad scope of iodo compounds was prepared in good to excellent yields. Furthermore, two multistep continuous-flow processes including either a halogen exchange/amidation or a halogen exchange/Mg–I exchange/nucleophilic addition sequence were established.

Arenes

X. Li, Y. Zhu, J. Shao, L. Chen, S. Zhao,
B. Wang, S. Zhang, Y. Shao, H.-L. Zhang,
X. Shao* ________ 267 – 271

Ring Reconstruction on a Trichalcogenasumanene Buckybowl: A Facile Approach to Donor–Acceptor-Type [5-6-7] Fused Planar Polyheterocycles

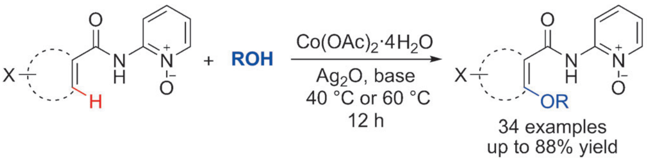


Bowled over: Oxidation of the electron-rich and bowl-shaped trichalcogenasumanenes by Oxone resulted in highly efficient ring-cleavage of the flanking benzene at room temperature. The successive ring-closure led to the creation of a series of donor–acceptor-type (D–A) [5-6-7] fused planar polyheterocycles, which show a strong red emission.

C–H Activation

L.-B. Zhang, X.-Q. Hao, S.-K. Zhang,
Z.-J. Liu, X.-X. Zheng, J.-F. Gong,
J.-L. Niu,* M.-P. Song* ________ 272 – 275

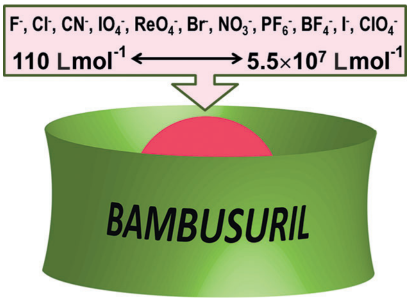
Cobalt-Catalyzed C(sp^2)–H Alkoxylation of Aromatic and Olefinic Carboxamides



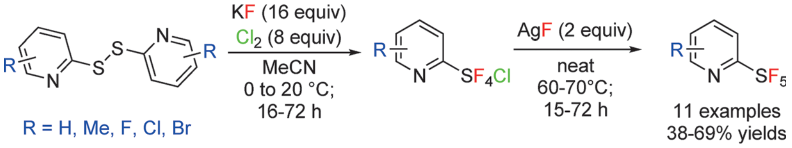
Alcohols in action: A wide range of alcohols and benzamide substrates functionalized with electron-rich or electron-poor substituents are tolerated in the title reaction. This practical reaction occurs under mild conditions.

Anion Receptors

One ring binds them all: A bambusuril macrocycle is able to selectively capture a large number of different inorganic anions in water. The high stability of the resulting inclusion complexes is due to multiple C—H···anion hydrogen bonding interaction in the hydrophobic cavity of the macrocycle.



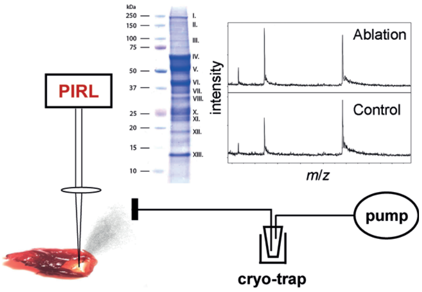
Synthetic Methods



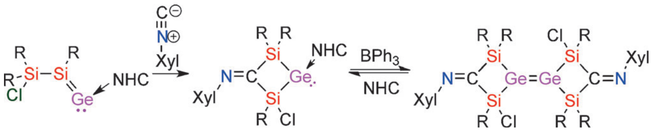
Excess oxidative fluorination of 2,2′-dipyridyl disulfides using a KF/Cl_2/MeCN system led to the formation of thirteen new 2-pyridylsulfur chlorotetrafluoride derivatives. These compounds were found to undergo further chlorine–fluorine exchange reactions with silver(I) fluoride enabling ready access to a series of substituted 2-pyridylsulfur pentafluorides.

Protein Extraction from Tissue

Proteins can be blasted out of intact tissues and into the gas phase in less than a millisecond with a picosecond IR laser (PIRL). The proteins are desorbed by impulsive excitation (DIVE) of intramolecular vibrational states of water molecules in the cell. PIRL-DIVE can be used to extract significant amounts of proteins ranging in size from a few kDa up to several MDa.



Ge–Ge Double Bonds

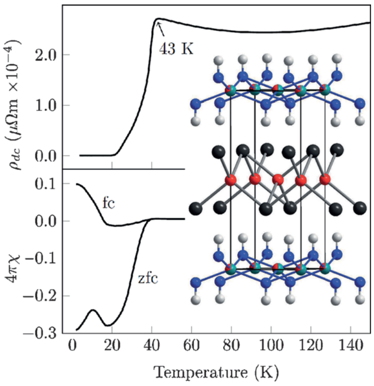


Geed up germanium: A multiply functionalized digermene is obtained under very mild reaction conditions from an N-heterocyclic carbene (NHC)-coordinated germanium(II) precursor. Both the imino and chloro functionalities are tolerated throughout the entire synthetic route. The starting material can be regenerated by the re-addition of the NHC.

Superconductivity and Ferromagnetism VIP

U. Pachmayr, F. Nitsche, H. Luetkens,
S. Kamusella, F. Brückner, R. Sarkar,
H.-H. Klauss, D. Johrendt* **293 – 297**

Coexistence of 3d-Ferromagnetism and Superconductivity in $[(Li_{1-x}Fe_x)OH](Fe_{1-y}Li_y)Se$



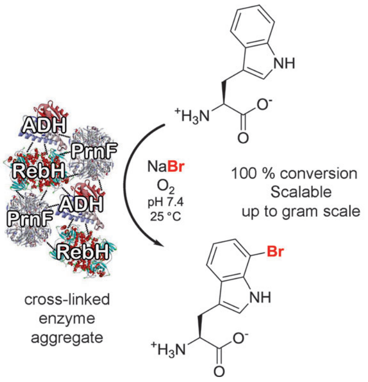
Opposites united: Superconductivity and ferromagnetism are antagonistic phenomena, and their coexistence is extremely rare. In $[(Li_{1-x}Fe_x)OH](Fe_{1-y}Li_y)Se$ superconductivity emerges in iron selenide layers at 43 K, while iron atoms in hydroxide layers exhibit ferromagnetic ordering at 10 K and generate a spontaneous vortex phase.

Enzymatic Halogenation

M. Frese, N. Sewald* **298 – 301**

Enzymatic Halogenation of Tryptophan on a Gram Scale

One for all, all for one: The combined immobilization of the tryptophan-7-halogenase RebH, a flavin reductase, and an alcohol dehydrogenase as a cross-linked enzyme aggregate leads to a solid multifunctional biocatalyst that can be used for an easily scalable regioselective synthesis of C7-halogenated tryptophan on a gram scale.

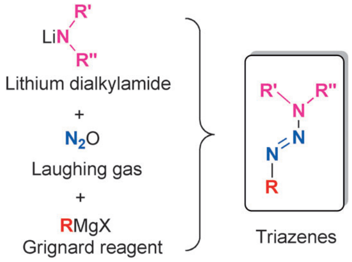


Nitrous Oxide

G. Kiefer, T. Riedel, P. J. Dyson,
R. Scopelliti, K. Severin* **302 – 305**

Synthesis of Triazenes with Nitrous Oxide

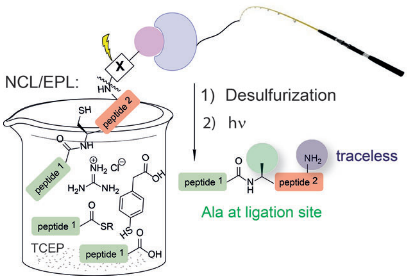
Synthesis with laughing gas: Triazenes can be obtained by the reaction of N_2O with secondary lithium amides and Grignard reagents. The new synthetic method allows access to triazenes with alkenyl and alkynyl substituents at the 1-position. Some of the alkynyl triazenes show selective anticancer activity in cell cultures.



Native Chemical Ligation

O. Reimann, C. Smet-Nocca,
C. P. R. Hackenberger* **306 – 310**

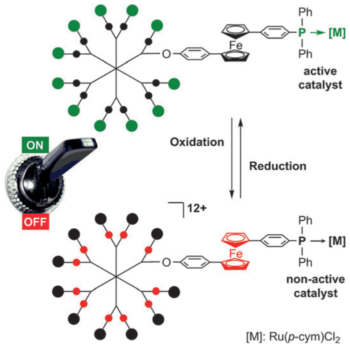
Traceless Purification and Desulfurization of Tau Protein Ligation Products



Fishing ligation products: Following a new method for traceless ligation, desulfurization, and purification, synthetic peptides equipped with photocleavable biotin are used in native chemical ligation (NCL) and expressed protein ligation (EPL) reactions. Pure, tag-free ligation products were obtained with a minimal time expenditure and used in an NCL-based synthesis of full-length human tau protein.

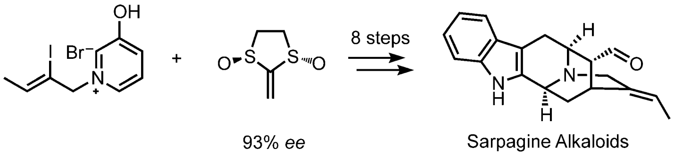
Redox-Switchable Catalysis

Inside Back Cover



Under control: Both monomeric and dendritic (see picture) ferrocenylphosphane ruthenium(II) catalysts were reversibly switched off and on by chemical oxidation and reduction during isomerization of the allylic alcohol 1-octen-3-ol. This outcome is mainly due to electronic communication between the redox-active unit and the catalytic center. Such redox control could facilitate the development of catalysts with orthogonal activity for different substrates.

Natural Product Synthesis



A general synthesis of sarpagine alkaloids proceeds through an eight-step sequence. The enantioselective total synthesis of (+)-vellosimine, (+)-*N*-methylvellosimine, and (+)-10-methoxyvellosimine has been accomplished without using protecting groups. A "privileged intermediate" is generated in the last step, from which all other members of the alkaloid family can be synthesized.

DOI: 10.1002/anie.201580114

Flashback: 50 Years Ago …

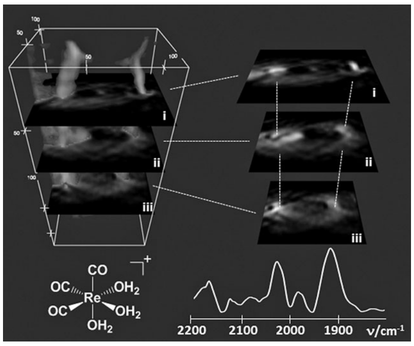
Richard Kuhn et al. reported on the stable triradical 1,3,5-tris-(1,5-diphenylverdazyl-3-yl)benzene, which contains ten conjugated six-membered rings and three unpaired electrons per molecule. Paramagnetic susceptibility and EPR measurements were used to confirm the radical nature of the compound, and it was noted that, unlike related biradicals, its electron spin remained unchanged down to 77 K.

Klaus Hafner et al. discussed the synthesis of pentaleno[2,1,6-def]heptalene. This molecule is a nonbenzenoid isomer of pyrene and can be described as either two pentalene and two heptalene units, or two azulene systems. The compound was of interest for investigating the connection between structure and aromaticity, however it was found that, despite its 4*n* π electrons, the compound was inert toward electrophilic reagents.

The issue also contained several Reviews on, at that time, contemporary topics in organic chemistry. Wolfgang Kirmse summarized the current knowledge of the intermediates of α-elimination reactions, including a discussion of radical and organometallic (carbanion) intermediates; Adolf W. Krebs discussed the properties of cyclopropenium compounds and cyclopropenones, which are Hückel aromatic (4*n* + 2) π-electron systems; and Gert Köbrich detailed the various possible mechanisms of elimination reactions from olefins.

Read more in Issue 1/1965.

Cellular Imaging

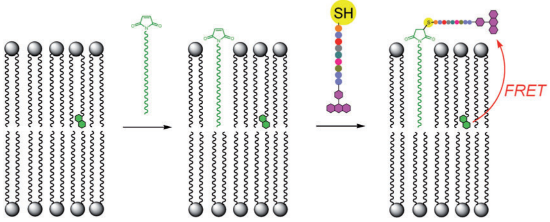


Now in 3D: Conventional 2D cell imaging methods are limited in their ability to associate specific information on the sample composition with subcellular structures. A new method, in which tilt-series infrared tomography is used with a standard benchtop infrared microscopy, provides quantitative information on the 3D distribution of molecular components based on the intrinsic contrast provided by the sample.

L. Quaroni,* M. Obst,* M. Nowak,
F. Zobi* ——— **318–322**

Three-Dimensional Mid-Infrared Tomographic Imaging of Endogenous and Exogenous Molecules in a Single Intact Cell with Subcellular Resolution

Membrane Recruitment



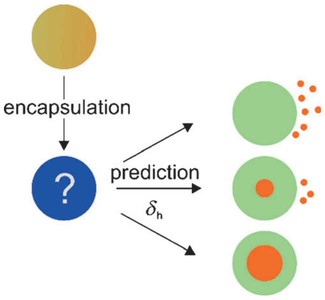
A lure for biomolecules: A palmitic acid derivative functionalized with a maleimide group serves to recruit sulfhydryl-containing biomolecules to membranes (see picture). The approach offers new possibilities for the preparation of biologically active liposomes and the manipulation of living cells.

I. Haralampiev, M. Mertens, R. Schwarzer,
A. Herrmann, R. Volkmer, P. Wessig,*
P. Müller* ——— **323–326**

Recruitment of SH-Containing Peptides to Lipid and Biological Membranes through the Use of a Palmitic Acid Functionalized with a Maleimide Group

Nanocapsules

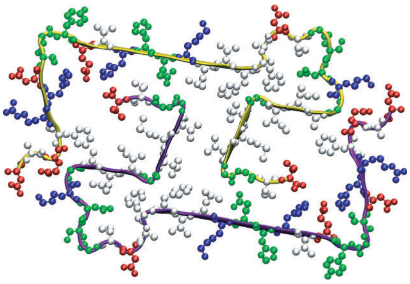
What's inside stays inside: The diffusion-barrier performance of polymeric nanocapsules, and thus their degree of loading, depends on the interactions between the polymer shell and the core material, which can be expressed by the Hansen solubility parameters. Using these parameters, in particular the hydrogen-bonding parameter δ_h, encapsulation efficiencies can be predicted and capsules with high diffusion barriers designed.



I. Hofmeister, K. Landfester,
A. Taden* ——— **327–330**

Controlled Formation of Polymer Nanocapsules with High Diffusion-Barrier Properties and Prediction of Encapsulation Efficiency

Amyloids



A fold not observed before: The atomic-resolution fibril structure of the Aβ1-40 peptide with the Osaka mutation (E22Δ), which is associated with early-onset Alzheimer's disease, differs substantially from all previously proposed models. In this complex structure the deletion mutation is found in a β turn.

A. K. Schütz, T. Vagt, M. Huber,
O. Y. Ovchinnikova, R. Cadalbert, J. Wall,
P. Güntert, A. Böckmann,*
R. Glockshuber,* B. H. Meier* **331–335**

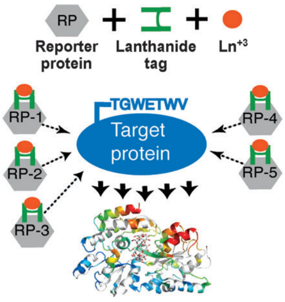
Atomic-Resolution Three-Dimensional Structure of Amyloid β Fibrils Bearing the Osaka Mutation

NMR Spectroscopy

A. R. Camacho-Zarco, F. Munari,
M. Wegstroth, W.-M. Liu, M. Ubbink,
S. Becker, M. Zweckstetter* ___ 336 – 339

Multiple Paramagnetic Effects through a Tagged Reporter Protein

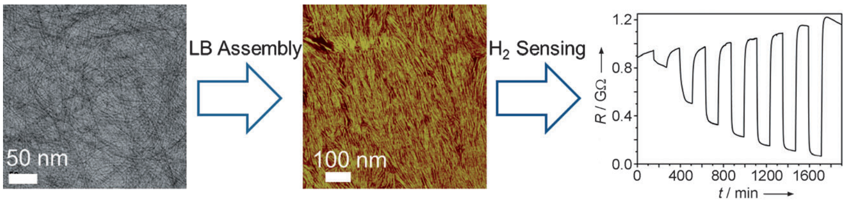
Information about the structure and dynamics of biomolecules can be obtained from paramagnetic effects. A lanthanoid tag can be attached to a reporter protein, which binds and then transmits paramagnetic information to the target protein. This approach provides access to a large number of paramagnetic effects based on independent molecular alignments in high-molecular-weight proteins with unknown 3D structure.



Nanowire Orientation

W. Cheng, Y. R. Ju, P. Payamyar, D. Primc,
J. Y. Rao, C. Willa, D. Koziej,
M. Niederberger* ___ 340 – 344

Large-Area Alignment of Tungsten Oxide Nanowires over Flat and Patterned Substrates for Room-Temperature Gas Sensing

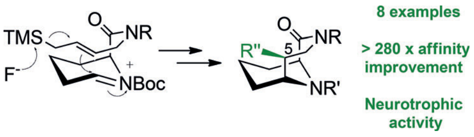


Sensing, down to the wire: A facile solution route provides ultrathin tungsten oxide nanowires (see picture, left) which can be aligned over a large area by the Langmuir–Blodgett technique (middle). The aligned tungsten oxide nanowire thin films exhibit excellent sensitivity to H_2 at room temperature (right).

Drug Design

S. Pomplun, Y. Wang, A. Kirschner,
C. Kozany, A. Bracher,
F. Hausch* ___ 345 – 348

Rational Design and Asymmetric Synthesis of Potent and Neurotrophic Ligands for FK506-Binding Proteins (FKBPs)

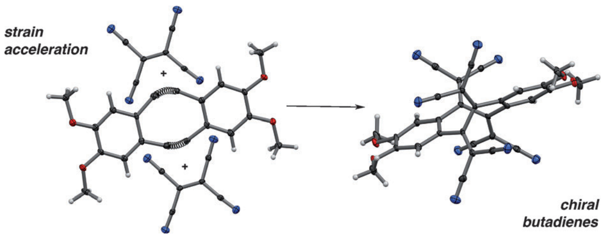


Designed to be potent: An asymmetric synthesis with an HF-driven N-acyliminium cyclization as key step afforded (*S*)-C^5-branched [4.3.1] aza-amide bicycles as a new class of highly potent and neurotrophic ligands for the psychiatric risk factor FKBP51. High resolution cocrystal structures confirmed the importance of the polar (*S*)-C^5 substituents, which led to a more than 280-fold affinity increase. TMS = trimethylsilyl.

Strained Molecules

M. Chiu,* B. H. Tchitchanov, D. Zimmerli,
I. A. Sanhueza, F. Schoenebeck,*
N. Trapp, W. B. Schweizer,
F. Diederich* ___ 349 – 354

Strain-Accelerated Formation of Chiral, Optically Active Buta-1,3-dienes

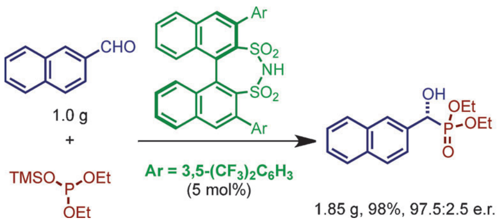


No strain, no gain: Strain induces up to 10^4-fold rate acceleration of the [2+2] cycloaddition–retroelectrocyclization reaction between tetracyanoethylene and dibenzo-fused cyclooctynes relative to unstrained systems. A rare example of a chiral, configurationally stable buta-1,3-diene was isolated. The activation barrier to racemization was determined experimentally to be up to 26 kcal mol^{-1} at 298 K.

Abramov Reaction

J. Guin, Q. Wang, M. van Gemmeren, B. List* ——— **355 – 358**

The Catalytic Asymmetric Abramov Reaction



- First catalytic enantioselective Abramov reaction
- Complementary to the established Pudovik reaction
- Mild reaction conditions
- High yields
- High enantioselectivities

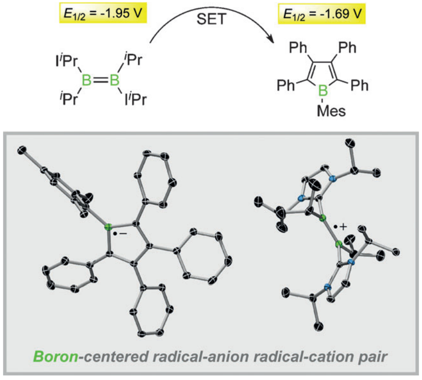
A chiral disulfonimide catalyst is used to achieve the first catalytic enantioselective Abramov reaction. Several functionalized α-hydroxy phosphonates were synthesized in good yields and with excellent enantiomeric ratios of up to $>$99:1. The process was shown to be scalable and up to 1 g of starting material could be employed under mild reaction conditions.

Boron Redox Chemistry

P. Bissinger, H. Braunschweig,* A. Damme, C. Hörl, I. Krummenacher, T. Kupfer ——— **359 – 362**

Boron as a Powerful Reductant: Synthesis of a Stable Boron-Centered Radical-Anion Radical-Cation Pair

The tailor-made diborene I*i*Pr·(*i*Pr)B=B-(*i*Pr)·I*i*Pr features an extremely electron-rich B–B double bond making it one of the most powerful neutral organic reductants known to date ($E_{1/2} = -1.95$ V). Its reducing power was successfully exploited in the synthesis of a very rare boron-centered radical-anion radical-cation pair by one-electron reduction of a borole, $MesBC_4Ph_4$. I*i*Pr = 1,3-diisopropylimidazol-2-ylidene.



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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