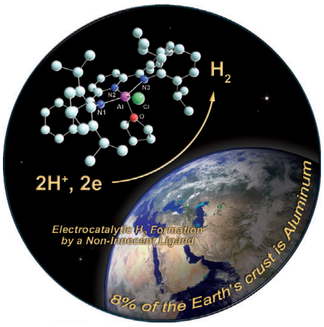
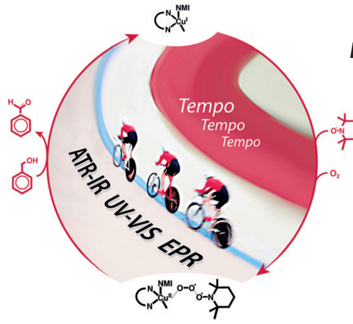
A magician …

… is looking into his crystal ball to read the future of a Lewis acid–base adduct. When his hand (an external stimulus) catches and rotates the phosphine oxide moiety, a highly active frustrated Lewis pair is formed in a process that is studied by S. Ogoshi, Y. Hoshimoto et al. in their Communication on page 11666 ff. This reactivation of frustration (and the high reactivity) is shown as a cracking of the crystal ball.

Electrocatalysis

In their Communication on page 11642 ff., L. A. Berben and E. J. Thompson show how a non-innocent ligand complex of aluminum electrocatalytically reduces protons to hydrogen gas. The proton- and electron-transfer processes are mediated by the redox-active ligand.



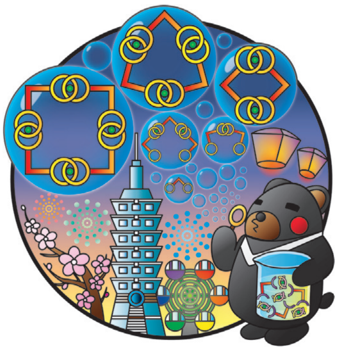


Homogeneous Catalysis

Operando ATR-IR, UV/Vis, and EPR spectroscopy are coupled by A. Brückner, U. Bentrup, J. Rabeah, and R. Stößer in their Communication on page 11791 ff. to unravel the mechanism of aerobic copper/TEMPO-catalyzed alcohol oxidation.

Dynamic Self-Assembly

In their Communication on page 11745 ff., S.-H. Chiu and co-workers describe the synthesis of dimeric, trimeric, and tetrameric cyclic [2]catenanes in a one-pot sodium-ion-templated process from a diamine and a tetraaldehyde.



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Spotlight on Angewandte's Sister Journals **11604 – 11607**

Author Profile

Annette Trunschke **11608**

"My favorite food is Japanese noodle soup, preferably with udon.
My favorite song is Wild Horses by The Rolling Stones …"
This and more about Annette Trunschke can be found on page 11608.

News

Royal Society of Chemistry Awards 2015 **11609**


P. J. Dyson


P. J. Pérez


P. Kukura


D. F. Hansen


M. I. Wallace


R. E. Morris


A. P. Davis


A. C. Balazs


S. J. Dalgarno


N. A. J. M. Sommerdijk

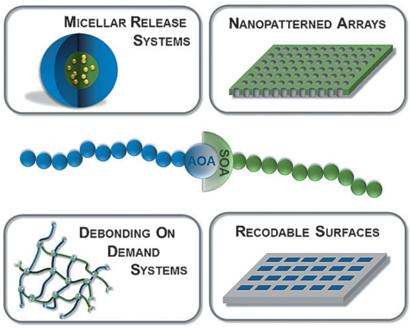

M. Barboiu

Highlights

Supramolecular Block Copolymers

L. Barner,*
C. Barner-Kowollik* ____ **11612 – 11614**

The Link that Lasts: A New Frontier in Supramolecular Block Copolymer Design



Lasting link: A supramolecular linkage between two parts of an amphiphilic block copolymer was developed that is sufficiently strong to allow phase-separation-driven nanopatterning as well as chromatographic characterization. The link can also be severed in response to a solvent trigger signal. This powerful approach will open new avenues for the production of self-healing materials, triggered-release systems, and reversible surface designs.

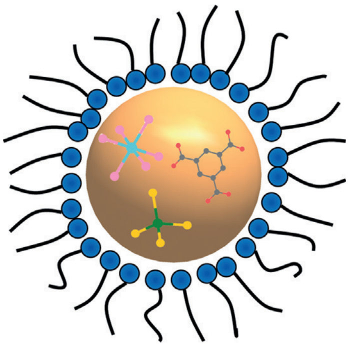
Minireviews

Materials Synthesis

W.-W. Xiong, Q. Zhang* _ **11616 – 11623**

Surfactants as Promising Media for the Preparation of Crystalline Inorganic Materials

Multifaceted media: Since surfactants can control the shape and size of micro-/nanoparticles, they are also able to direct the growth of bulk crystals. Recent developments in the use of surfactants in the preparation of crystalline inorganic materials, including chalcogenides, metal–organic frameworks, and zeolite analogues, are summarized in this Minireview.



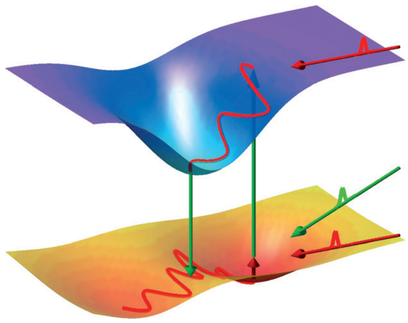
Reviews

Spectroscopic Methods

L. J. G. W. van Wilderen,*
J. Bredenbeck* ______ **11624 – 11640**

From Ultrafast Structure Determination to Steering Reactions: Mixed IR/Non-IR Multidimensional Vibrational Spectroscopies

Finger on the pulse: Combining IR with non-IR pulses in multidimensional vibrational spectroscopy creates techniques with possibilities far beyond those of IR experiments alone. These include powerful tools for studying photochemistry, dynamics at surfaces and interfaces, as well as non-equilibrium structural dynamics. This Review discusses important differences between useful pulse sequences and gives examples of their application.



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ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

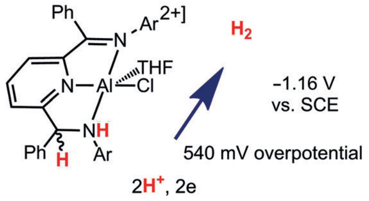
Electrocatalysis

E. J. Thompson,
L. A. Berben* ________ 11642 – 11646

Electrocatalytic Hydrogen Production by an Aluminum(III) Complex: Ligand-Based Proton and Electron Transfer

Frontispiece

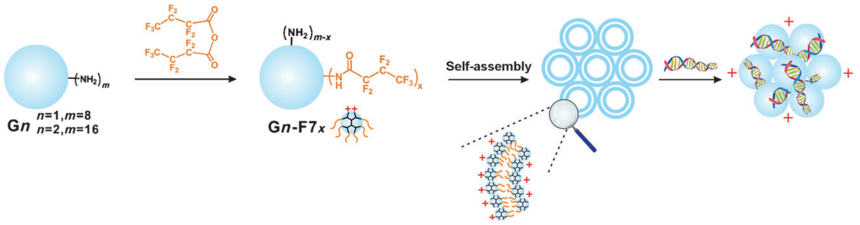
Two in one: Proton and electron transfer by a complex comprising Al^{3+} and a redox-active iminopyridine ligand promotes electrocatalytic H_2 evolution. The Al^{3+} center brings the reduction potential of the ligand into an accessible range for low-overpotential proton production. The proposed mechanism involves two protonation events at the ligand and a subsequent two-electron reduction to liberate hydrogen (see figure).



Gene Delivery

H. Wang, Y. Wang, Y. Wang, J. Hu, T. Li,
H. Liu, Q. Zhang,
Y. Cheng* ________ 11647 – 11651

Self-Assembled Fluorodendrimers Combine the Features of Lipid and Polymeric Vectors in Gene Delivery



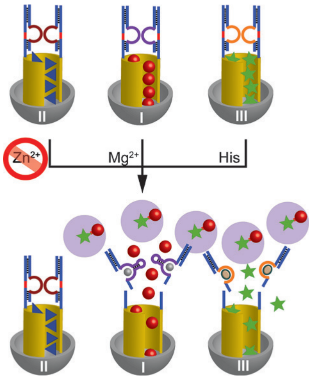
Low-molecular-weight fluorodendrimers are used to generate carriers for gene delivery. These materials self-assemble into uniform nanospheres and allow for efficient transfection at low charge ratios and very low DNA doses. They exhibit minimal cytotoxicity.

DNA Nanotechnology

D. Balogh, M. A. Aleman Garcia,
H. B. Albada,* I. Willner* 11652 – 11656

Programmed Synthesis by Stimuli-Responsive DNAzyme-Modified Mesoporous SiO_2 Nanoparticles

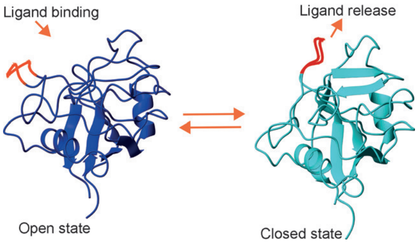
Cofactor-dependent DNAzymes trigger the selective unlocking of a mixture of loaded mesoporous SiO_2 nanoparticles. This results in the programmed synthesis of click-chemistry products.



Protein Structure

C. N. Chi, B. Vögeli, S. Bibow, D. Strotz,
J. Orts, P. Güntert,
R. Riek* ________ 11657 – 11661

A Structural Ensemble for the Enzyme Cyclophilin Reveals an Orchestrated Mode of Action at Atomic Resolution

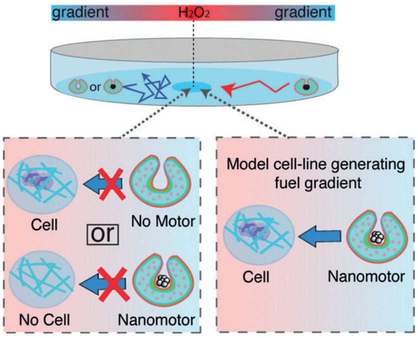


Time may change me: An experimental restraint driven two-state ensemble of the prototypical enzyme cyclophilin was determined. The results reveal the presence of an open and a closed state, which is indicative of large-scale correlated motion. In the open state, the catalytic site is preorganized for catalysis, thus suggesting the mechanism of action to be conformational sampling, while the ligand-binding loop appears to act through an induced-fit mechanism.

Nanomedicine

F. Peng, Y. Tu, J. C. M. van Hest,*
D. A. Wilson* ________ **11662 – 11665**

Self-Guided Supramolecular Cargo-Loaded Nanomotors with Chemotactic Behavior towards Cells



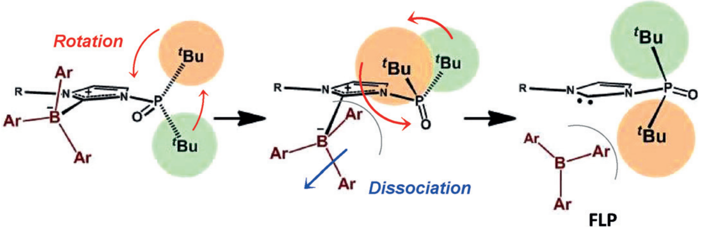
Chemotactic nanoparticles: Platinum-loaded polystyrene nanoparticles were shown to exhibit directional movement along hydrogen peroxide gradients in both static and flowing systems. Furthermore, the nanoparticles could encapsulate the model cancer drug doxorubicin and migrate towards hydrogen peroxide producing neutrophil cells, suggesting such nanoparticles could be used as drug delivery vehicles.

Frustrated Lewis Pairs

Y. Hoshimoto,* T. Kinoshita, M. Ohashi,
S. Ogoshi* ________ **11666 – 11671**

A Strategy to Control the Reactivation of Frustrated Lewis Pairs from Shelf-Stable Carbene Borane Complexes

Front Cover



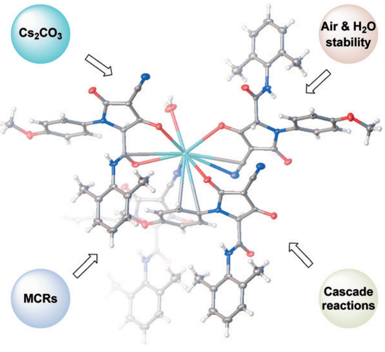
Frustration under control: Imidazolylidenes with a phosphine oxide substituent on one of the nitrogen atoms can undergo drastic changes to the spatial environment surrounding their carbene center through rotation of the phosphine oxide moiety. Depending on the orientation of this group, either classical Lewis adducts or frustrated Lewis pairs (FLPs) are formed upon addition of $B(C_6F_5)_3$.

Multicomponent Reactions

G. Martinez-Ariza, M. Ayaz, S. A. Roberts,
W. A. Rabanal-León, R. Arratia-Pérez,
C. Hulme* ________ **11672 – 11676**

The Synthesis of Stable, Complex Organocesium Tetramic Acids through the Ugi Reaction and Cesium-Carbonate-Promoted Cascades

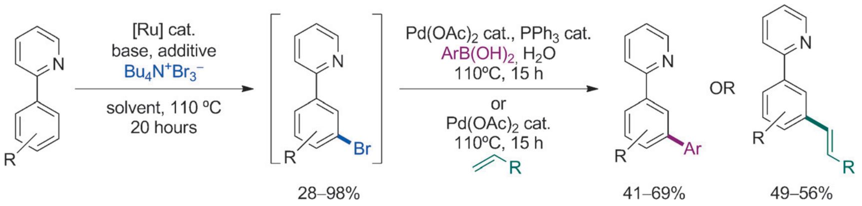
Cascades, cesium, and complexity: Two structurally unique organocesium carbanionic tetramic acids have been synthesized through expeditious and novel cascade reactions of strategically functionalized Ugi skeletons delivering products with two points of potential diversification. This is the first report of the use of multicomponent reactions and subsequent cascades to access unprecedented complex organocesium architectures.



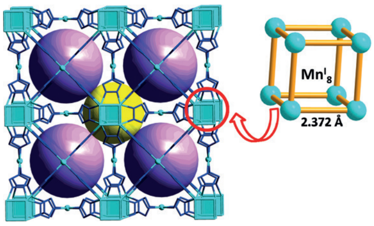
C–H Activation

C. J. Teskey, A. Y. W. Lui,
M. F. Greaney* ________ **11677 – 11680**

Ruthenium-Catalyzed *meta*-Selective C–H Bromination



Taking position: 2-Phenylpyridines undergo *meta*-selective bromination using tetrabutylammonium tribromide under ruthenium catalysis, thus affording products that are highly predisposed to further derivatization. The bromination can be combined with arylation and alkenylation chemistry to access *meta*-arylated and *meta*-alkenylated products, respectively, in a one-pot operation.



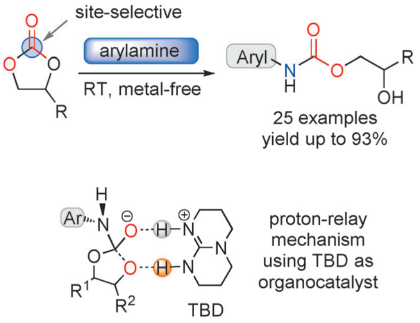
A cubic [Mn^{I}_8] cluster based metal–organic framework (MOF) with multicentered Mn^{I}—Mn^{I} bonds and +1 oxidation state of manganese has been synthesized and characterized. This MOF features the shortest Mn^{I}—Mn^{I} bond of 2.372 Å and is antiferromagnetic. Theoretical studies reveal a dual cubic aromaticity that arises from the extensive electron delocalization over the [Mn^{I}_8] cube.

Metal–Organic Frameworks

H.-C. Hu, H.-S. Hu, B. Zhao,* P. Cui,
P. Cheng, J. Li* ———— **11681 – 11685**

Metal–Organic Frameworks (MOFs) of a Cubic Metal Cluster with Multicentered Mn^{I}—Mn^{I} Bonds

---



By relay: The previously unknown site-selective attack of arylamines on cyclic carbonates to deliver N-aryl carbamates as the principal product is reported. The organocatalyst TBD guides an effective proton-relay process, thus mediating a chemoselective formation of the carbamate target under extremely mild reaction conditions. The new methodology represents a sustainable, cheap, and attractive process towards these important N-aryl carbamate synthons.

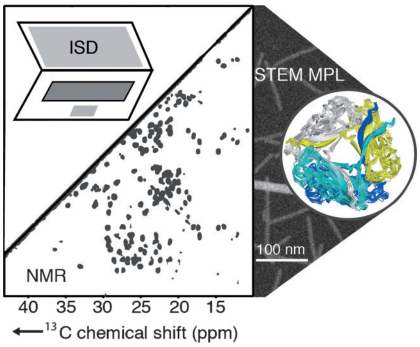
Organocatalysis

W. Guo, J. González-Fabra,
N. A. G. Bandeira, C. Bo,
A. W. Kleij* ———— **11686 – 11690**

A Metal-Free Synthesis of N-Aryl Carbamates under Ambient Conditions

---

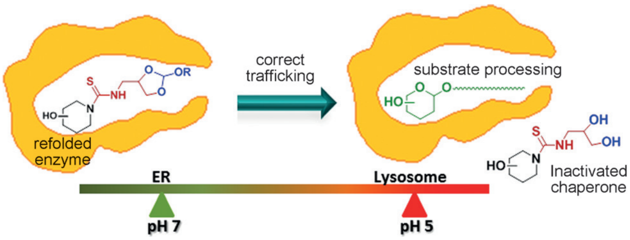
Atomic precision was possible in the elucidation of the hybrid structure of a bacterial filamentous protein assembly by a combination of solid-state and solution NMR spectroscopy, STEM measurements, and iterative modeling (see picture; ISD refers to the Inferential Structure Determination software). This approach enabled accurate identification of the intermolecular interfaces that contribute to the assembly and stability of the type 1 pilus.



Protein Structures

B. Habenstein, A. Loquet, S. Hwang,
K. Giller, S. K. Vasa, S. Becker,
M. Habeck,* A. Lange* — **11691 – 11695**

Hybrid Structure of the Type 1 Pilus of Uropathogenic *Escherichia coli*



pH-Responsive chaperones for rescuing mutant lysosomal glycosidases were developed by incorporating an acid-labile orthoester into sp^2-iminosugar conjugates. In the endoplasmic reticulum (ER; pH 7), the chaperone binds to the mutant enzyme and promotes correct folding and trafficking. In the lysosome (pH 5), fast hydrolysis of the orthoester leads to inactivation of the chaperone.

Misfolded Proteins

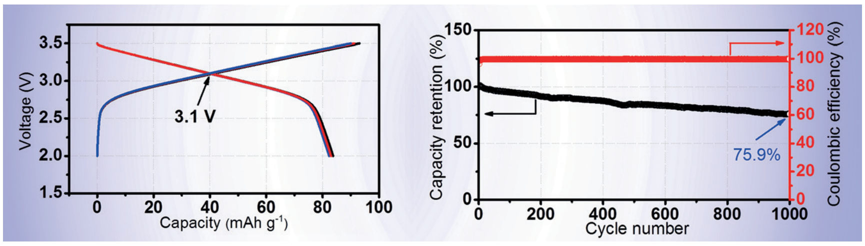
T. Mena-Barragán, A. Narita, D. Matias,
G. Tiscornia, E. Nanba, K. Ohno,
Y. Suzuki, K. Higaki,*
J. M. Garcia Fernández,*
C. Ortiz Mellet* ———— **11696 – 11700**

pH-Responsive Pharmacological Chaperones for Rescuing Mutant Glycosidases

Sodium Full Cells

S. H. Guo, P. Liu, Y. Sun, K. Zhu, J. Yi, M. W. Chen, M. Ishida, H. S. Zhou* ———— **11701 – 11705**

A High-Voltage and Ultralong-Life Sodium Full Cell for Stationary Energy Storage



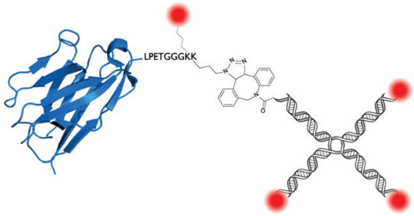
In full flow: A sodium full cell based on $Na_{0.66}Ni_{0.17}Co_{0.17}Ti_{0.66}O_2$ as both the cathode and anode has been designed. It exhibits the highest average voltage of approximately 3.10 V in the symmetric cells and the longest cycle life (75.9 % capacity retention after 1000 cycles) in all reported sodium full cells, and also shows a usable capacity and superior rate capability.

Imaging Agents

Z. Li, C. S. Theile, G.-Y. Chen, A. M. Bilate, J. N. Duarte, A. M. Avalos, T. Fang, R. Barberena, S. Sato, H. L. Ploegh* ———— **11706 – 11710**

Fluorophore-Conjugated Holliday Junctions for Generating Super-Bright Antibodies and Antibody Fragments

Many hands make light work: Holliday junctions with fluorophores (red) conjugated at three of the four arms can be used to attach multiple fluorophores to both single-domain and full-sized antibodies (blue) with sufficient spacing to avoid self-quenching. The resulting conjugates showed improved fluorescence yields over those of singly fluorophore-conjugated antibodies without adversely affecting antigen binding.

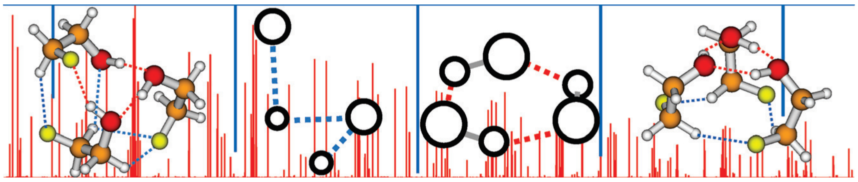


Hydrogen Bonding

J. Thomas, X. Liu, W. Jäger, Y. Xu* ———— **11711 – 11715**

Unusual H-Bond Topology and Bifurcated H-Bonds in the 2-Fluoroethanol Trimer

Inside Cover

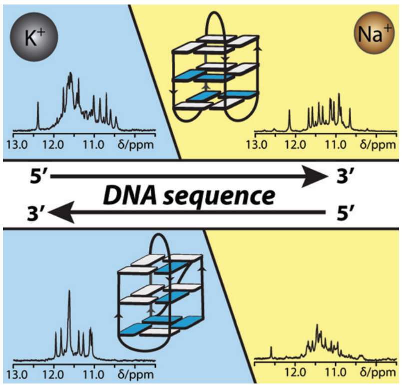


The unexpected: The trimer of 2-fluoroethanol demonstrates a striking case of chirality-induced H-bond topology switching. It strongly favors a heterochiral arrangement stabilized by both normal and bifurcated H-bonds, rather than the common binding topology with a cyclic OH⋯OH bonded ring that is adopted by trimers of water and other related alcohol molecules. The role of transient chirality and the strength of the bifurcated H-bonds were investigated.

G-Quadruplexes

M. Marušič, J. Plavec* ———— **11716 – 11719**

The Effect of DNA Sequence Directionality on G-Quadruplex Folding

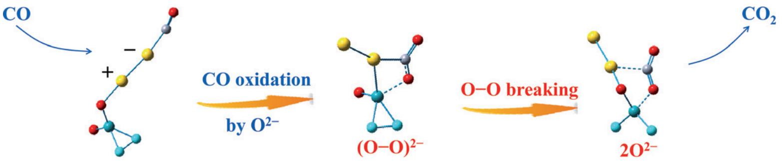


In reverse: Sequence inversion in G-rich oligonucleotides from the 5′→3′ to the 3′→5′ direction has a substantial effect on the thermal stability and number of structures formed, while the type of G-quadruplex fold is in fact determined by the type of cation present. CD, UV, and NMR spectroscopy were used to provide new insights into the structural preferences of important classes of G-rich DNA.

Cluster Compounds

L.-N. Wang, Z.-Y. Li, Q.-Y. Liu, J.-H. Meng, S.-G. He,* T.-M. Ma* ____ 11720 – 11724

CO Oxidation Promoted by the Gold Dimer in $Au_2VO_3^-$ and $Au_2VO_4^-$ Clusters

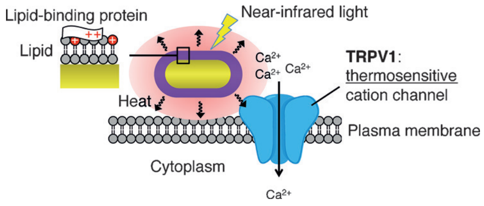


Gold in action: The cluster $Au_2VO_4^-$, doped with a gold dimer, can activate the peroxide species O_2^{2-} bonded to the vanadium center to oxidize CO molecules under thermal collision conditions. The CO oxidation mechanism parallels similar behavior for oxide-supported gold catalysts.

Photothermal Effects

H. Nakatsuji, T. Numata, N. Morone, S. Kaneko, Y. Mori, H. Imahori, T. Murakami* ________ 11725 – 11729

Thermosensitive Ion Channel Activation in Single Neuronal Cells by Using Surface-Engineered Plasmonic Nanoparticles

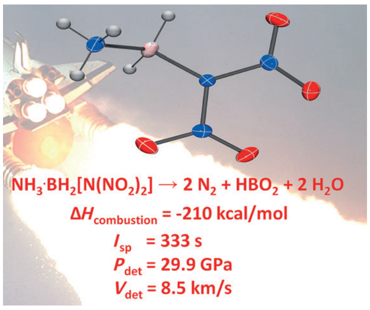


Hot membranes: A non-disruptive plasma membrane heating method employs gold nanorods (AuNRs) coated with a cationic protein/lipid complex. Under near-infrared illumination, these AuNRs induce highly localized photothermal heat generation in intact neuronal cells without membrane damage, enabling Ca^{2+} influx solely by activation of the thermosensitive cation channel TRPV1.

Energetic Materials

G. Bélanger-Chabot, M. Rahm, R. Haiges, K. O. Christe* ________ 11730 – 11734

Ammonia–(Dinitramido)boranes: High-Energy-Density Materials

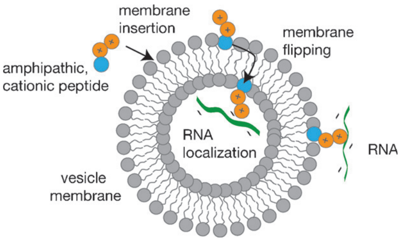


Boranes pack a punch: Ammonia–(dinitramido)boranes were prepared from dinitroamine and ammonia–borane. Ammonia–mono(dinitramido)borane is a perfectly oxygen-balanced high-energy-density material and is the first structurally characterized Group 13 dinitramido compound. P_{det} = detonation pressure and V_{det} = detonation velocity of the compound as an explosive; I_{sp} = specific impulse of the compound as a propellant.

Origin of Life

N. P. Kamat, S. Tobé, I. T. Hill, J. W. Szostak* ________ 11735 – 11739

Electrostatic Localization of RNA to Protocell Membranes by Cationic Hydrophobic Peptides

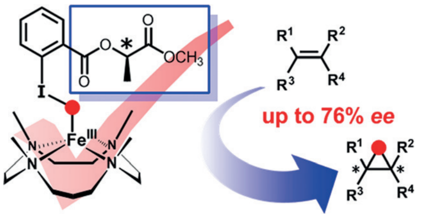


RNA–membrane association: Simple peptides (as small as three amino acids) can localize RNA to model membrane systems by electrostatic interactions. Microscopy studies showed that peptides can cross vesicle membranes to localize encapsulated RNA.

Epoxidation Reactions

B. Wang, Y.-M. Lee, M. S. Seo,
W. Nam* ______ 11740 – 11744

Mononuclear Nonheme Iron(III)-Iodosylarene and High-Valent Iron-Oxo Complexes in Olefin Epoxidation Reactions



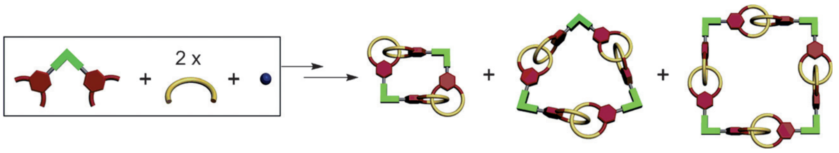
On active duty: High-spin iron(III)-iodosylarene complexes epoxidize olefins with high stereospecificity and enantioselectivity. The iron(III)-iodosylarene species, not high-valent iron(IV)- and iron(V)-oxo species, are the active oxidants in catalytic olefin epoxidation reactions. The present results resolve the long-standing controversy on the one oxidant versus multiple oxidants hypothesis in oxidation reactions.

Dynamic Self-Assembly

Y.-W. Wu, S.-T. Tung, C.-C. Lai, Y.-H. Liu,
S.-M. Peng, S.-H. Chiu* _ 11745 – 11749

Cyclic [2]Catenane Dimers, Trimers, and Tetramers

Back Cover



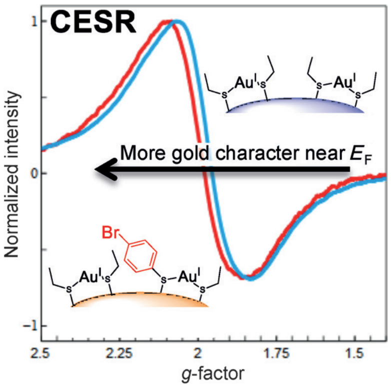
Only with sodium: Dimeric, trimeric, and tetrameric cyclic [2]catenanes are formed through sodium-ion-templated dynamic imine formation from a diamine and a tetraaldehyde. Reduction of the labile imino bonds followed by methylation enabled the isolation and characterization of the oligomeric cyclic [2]catenanes as stable, covalently linked compounds.

Gold Nanoparticles

A. Cirri, A. Silakov,
B. J. Lear* ______ 11750 – 11753

Ligand Control over the Electronic Properties within the Metallic Core of Gold Nanoparticles

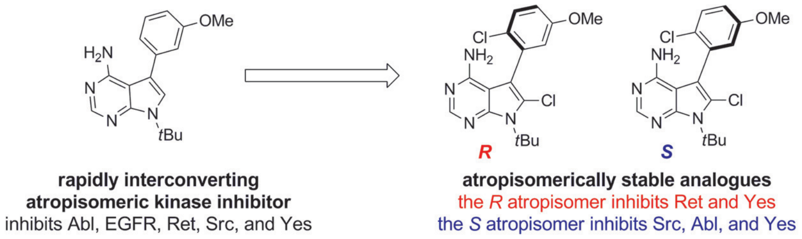
Good as gold: The surface chemistry of gold nanoparticles (AuNPs) is shown to influence the behavior of electrons within the metallic core. Conduction electron spin resonance (CESR) spectra and surface plasmon resonance bands for AuNPs are sensitive to ligand exchange of hexanethiol for 4-bromothiophenol on the surface of the NPs, demonstrating that the chemical nature of the ligand controls the valence band structure of AuNPs.



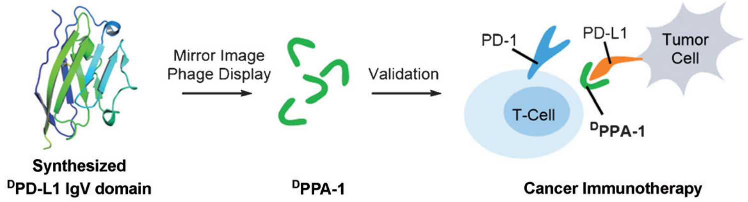
Inhibitors

D. E. Smith, I. Marquez,
M. E. Lokensgard, A. L. Rheingold,
D. A. Hecht,
J. L. Gustafson* ______ 11754 – 11759

Exploiting Atropisomerism to Increase the Target Selectivity of Kinase Inhibitors



Rigidified: A series of conformationally stable kinase inhibitors were synthesized, and the effect of atropisomerism on kinase selectivity was assessed. The use of these inhibitors was found to lead to improved selectivity compared with the rapidly interconverting parent compounds.



Protein chemical synthesis and mirror-image phage display were combined to develop a proteolysis-resistant D-peptide antagonist (^{D}PPA-1) which targets the immune checkpoint protein PD-L1 (the ligand for PD-1, the programmed cell death protein 1). ^{D}PPA-1 was found to inhibit the PD-1/PD-L1 protein–protein interaction at the cellular level. IgV = immunoglobulin-like variable.

Cancer Immunotherapy

H.-N. Chang, B.-Y. Liu, Y.-K. Qi, Y. Zhou, Y.-P. Chen, K.-M. Pan, W.-W. Li, X.-M. Zhou, W.-W. Ma, C.-Y. Fu, Y.-M. Qi, L. Liu,* Y.-F. Gao* ______ **11760 – 11764**

Blocking of the PD-1/PD-L1 Interaction by a D-Peptide Antagonist for Cancer Immunotherapy

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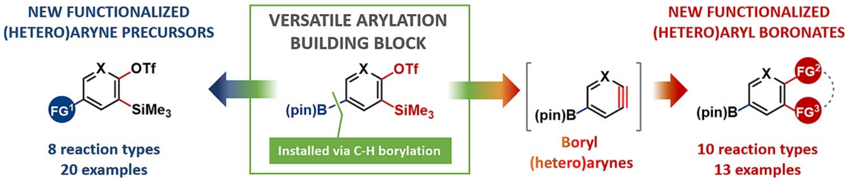

Ready for a complete makeover: As building blocks for arylation, (pinacolato)boryl *ortho*-silyl (hetero)aryl triflates (see structure; X = C, N) showed unique versatility by reacting chemoselectively as boronates or (hetero)arynes in a broad range of transformations. This approach offers valuable possibilities for the functionalization of both aryne precursors and aryl boronates without the use of specialized protecting groups.

Synthetic Methods

E. Demory, K. Devaraj, A. Orthaber, P. J. Gates, L. T. Pilarski* **11765 – 11769**

Boryl (Hetero)aryne Precursors as Versatile Arylation Reagents: Synthesis through C–H Activation and Orthogonal Reactivity

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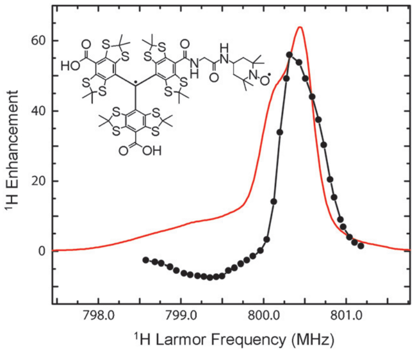

Radical design: A series of biradicals consisting of a nitroxide radical chemically tethered to a trityl radical were employed for cross-effect dynamic nuclear polarization at 211, 600, and 800 MHz. The relatively strong exchange interaction between the trityl and nitroxide moieties determined the field strength at which the enhancement is optimized, and yielded a record ^{1}H NMR signal enhancement of 65 at 800 MHz.

Solid-State NMR Spectroscopy

G. Mathies,* M. A. Caporini, V. K. Michaelis, Y. Liu,* K.-N. Hu, D. Mance, J. L. Zweier, M. Rosay, M. Baldus, R. G. Griffin* **11770 – 11774**

Efficient Dynamic Nuclear Polarization at 800 MHz/527 GHz with Trityl-Nitroxide Biradicals

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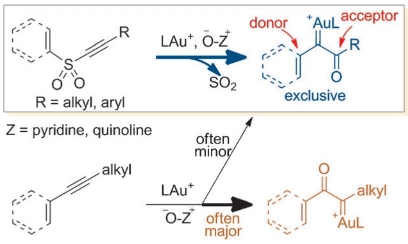
Accept it: A desulfonylative approach was developed to regiospecifically access these underexplored acyl gold carbenes from either alkynyl aryl/alkenyl sulfones or alkynyl sulfonate substrates. The reactivities of these donor- and acceptor-substituted carbenes are examined.



Carbenes

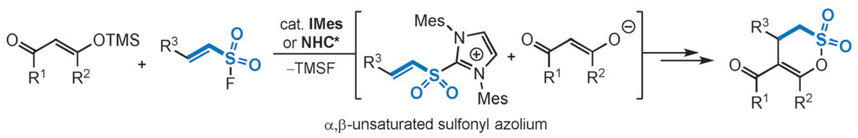
H. Chen, L. Zhang* ______ **11775 – 11779**

A Desulfonylative Approach in Oxidative Gold Catalysis: Regiospecific Access to Donor-Substituted Acyl Gold Carbenes

Organocatalysis

A. Ungureanu, A. Levens, L. Candish,
D. W. Lupton* ———— 11780 – 11784

N-Heterocyclic Carbene Catalyzed Synthesis of δ-Sultones via α,β-Unsaturated Sulfonyl Azolium Intermediates

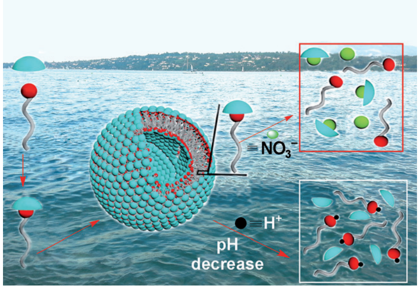


A new intermediate: The coupling of α,β-unsaturated sulfonyl fluorides with silyl enol ethers in the presence of N-heterocyclic carbenes provides δ-sultones in good yields. Various mechanistic studies indicate the formation of an α,β-unsaturated sulfonyl azolium intermediate.

Supramolecular Amphiphiles

Q. He, Y.-F. Ao, Z.-T. Huang,
D.-X. Wang* ———— 11785 – 11790

Self-Assembly and Disassembly of Vesicles as Controlled by Anion–π Interactions



May the best guest win: Supramolecular amphiphiles formed by anion–π interactions between an anionic amphiphile (anionic part in red in the picture) and a macrocyclic π system (light blue) underwent self-assembly into vesicles in water. The controlled disassembly of the vesicles was promoted by competing anions or a decrease in the pH value (see picture).

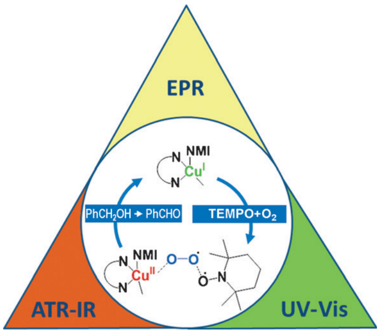
Homogeneous Catalysis

J. Rabeah,* U. Bentrup,* R. Stößer,
A. Brückner* ———— 11791 – 11794

Selective Alcohol Oxidation by a Copper TEMPO Catalyst: Mechanistic Insights by Simultaneously Coupled Operando EPR/UV-Vis/ATR-IR Spectroscopy

Inside Back Cover

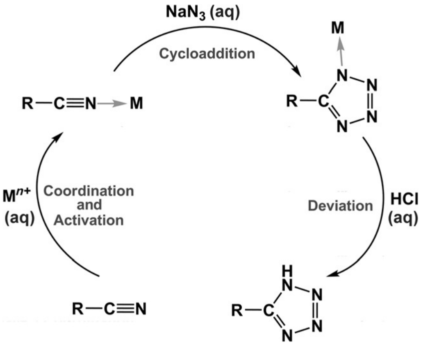
All good things come in threes: Simultaneous operando EPR/UV-vis/ATR-IR spectroscopy provides new mechanistic insights in TEMPO-catalyzed aerobic alcohol oxidation. TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.



Tetrazole Synthesis

D. C. Zhong,* Y. Q. Wen, J. H. Deng,
X. Z. Luo,* Y. N. Gong,
T. B. Lu* ———— 11795 – 11799

Uncovering the Role of Metal Catalysis in Tetrazole Formation by an In Situ Cycloaddition Reaction: An Experimental Approach

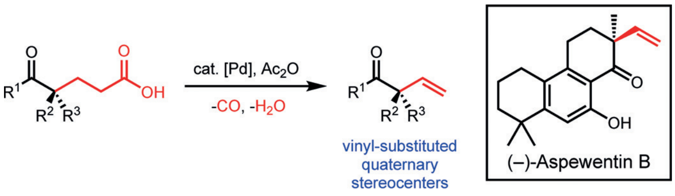


A key role: Using an experimental approach, the role of metal catalysis has been investigated in the in situ cycloaddition reaction of nitrile with azide to form tetrazoles. X-ray crystallography and IR spectroscopy are used to show that the metal species acts as a catalyst, activating the cyano group in the nitrile-containing reagent by a coordinative interaction.

Natural Products

Y. Liu, S. C. Virgil, R. H. Grubbs,*
B. M. Stoltz* ______ 11800 – 11803

Palladium-Catalyzed Decarbonylative Dehydration for the Synthesis of α-Vinyl Carbonyl Compounds and Total Synthesis of (−)-Aspewentins A, B, and C



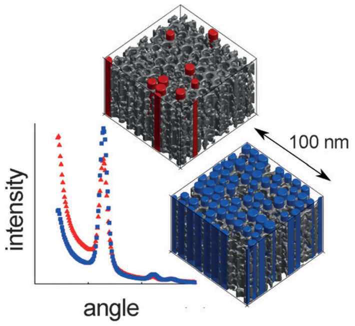
Vinyl unveiled: It is described that δ-oxocarboxylic acids can serve as masked vinyl compounds and be unveiled by Pd-catalyzed decarbonylative dehydration to enable the α-vinylation of carbonyl compounds to form a quaternary stereocenter. A variety of α-vinyl quaternary carbonyl compounds are obtained in good yields, and an application in the first enantioselective total synthesis of (−)-aspewentins A–C is demonstrated.

Nanoparticles

C. J. Gommes,* G. Prieto, J. Zecevic,
M. Vanhalle, B. Goderis, K. P. de Jong,
P. E. de Jongh* ______ 11804 – 11808

Mesoscale Characterization of Nanoparticles Distribution Using X-ray Scattering

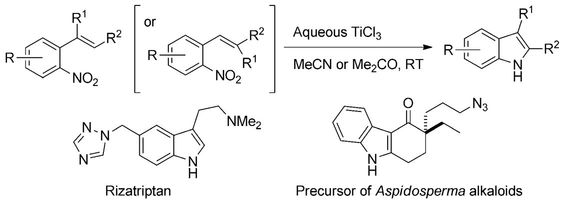
The background is the data: The properties of many materials depend on the spatial distribution of nanoparticles at the mesoscopic scale. The latter distribution can be characterized quantitatively from the background intensity in X-ray scattering patterns (see picture). Compared to electron tomography, this procedure enhances the sampling by twelve orders of magnitude, and it offers new prospects for in situ studies.



Synthetic Methods

S. Tong, Z. Xu, M. Mamboury, Q. Wang,
J. Zhu* ______ 11809 – 11812

Aqueous Titanium Trichloride Promoted Reductive Cyclization of o-Nitrostyrenes to Indoles: Development and Application to the Synthesis of Rizatriptan and Aspidospermidine

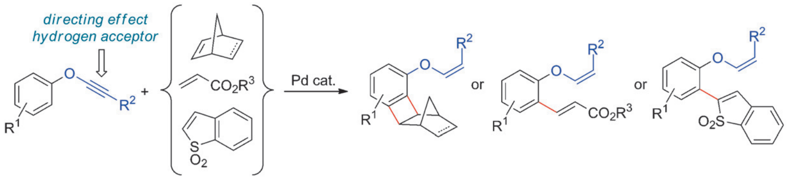


Mild and efficient treatment of *o*-nitrostyrenes with aqueous $TiCl_3$ solution at room temperature afforded indoles through a formal reductive C(sp^2)–H amination process. A concise synthesis of a marketed drug (rizatriptan) and a formal total synthesis of aspidospermidine featuring this novel N-heterocyclization process are reported.

C–C Coupling

Y. Minami,* T. Kodama,
T. Hiyama* ______ 11813 – 11816

Dehydrogenative Carbon–Carbon Bond Formation Using Alkynyloxy Moieties as Hydrogen-Accepting Directing Groups

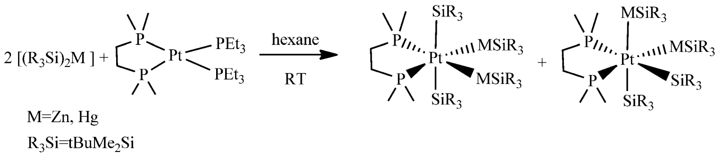


Alkyne into alkene: A palladium catalyst enables dehydrogenative C–C bond-forming reactions between alkynyl aryl ethers and alkenes or heteroarenes. The presence of the alkynyloxy group is key for these transformations as it acts as a directing group for the site-selective cleavage of two C–H bonds as well as an acceptor for the released hydrogen.

Bond Cleavage

Y. Kratish, G. Molev, A. Kostenko,
D. Sheberla, B. Tumanskii,
M. Botoshansky, S. Shimada,
D. Bravo-Zhivotovskii,*
Y. Apeloig* ______ **11817 – 11821**

Activation of Homolytic Si–Zn and Si–Hg Bond Cleavage, Mediated by a Pt^0 Complex, via Novel Pt–Zn and Pt–Hg Compounds

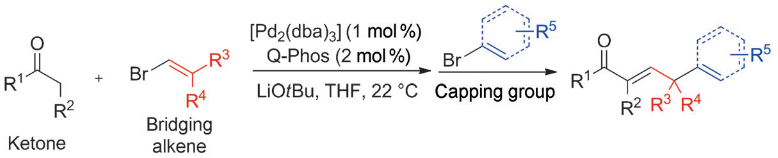


SiM City: The thermally stable [(tBu-Me$_2$Si)$_2$M] (M = Zn, Hg) generate R$_3$Si$^\bullet$ radicals in the presence of [(dmpe)Pt(PEt$_3$)$_2$]. The enhancing effect of the Pt complex on the homolytic cleavage of the Si–M bonds in [(tBuMe$_2$Si)$_2$M] is mediated by formation of octahedral hexacoordinate Pt–M trinuclear complexes.

Cross-Coupling

M. Grigalunas, P.-O. Norrby, O. Wiest,
P. Helquist* ______ **11822 – 11825**

Single-Flask Multicomponent Palladium-Catalyzed α,γ-Coupling of Ketone Enolates: Facile Preparation of Complex Carbon Scaffolds

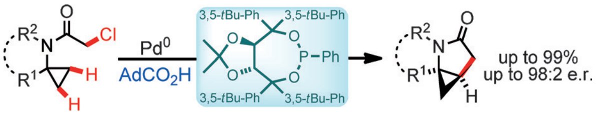


Building bridges: The title reaction was developed for the construction of γ-substituted α,β-unsaturated ketones under mild reaction conditions. High levels of regioselectivity and control of incorporation of reaction components are exhibited, thus producing complex scaffolds in a single-flask procedure. dba = dibenzylideneacetone, THF = tetrahydrofuran, Q-Phos = 1-di-*tert*-butylphosphino-1′,2′,3′,4′,5′-pentaphenylferrocene.

C–H Activation

J. Pedroni, N. Cramer* ___ **11826 – 11829**

Chiral γ-Lactams by Enantioselective Palladium(0)-Catalyzed Cyclopropane Functionalizations

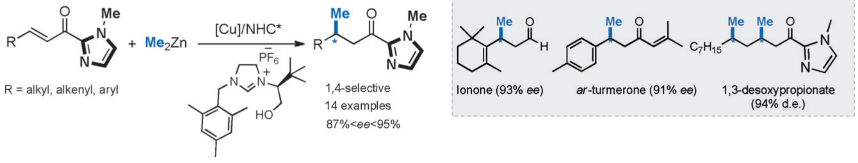


Bulk up: An enantioselective C–H functionalization strategy is used to access cyclopropane-fused γ-lactams from readily accessible chloroacetamide substrates. A bulky Taddol phosphonite ligand in combination with adamantane-1-carboxylic acid as a cocatalyst provides the γ-lactams in excellent yields and enantioselectivities.

Asymmetric Catalysis

S. Drissi-Amraoui, M. S. T. Morin,
C. Crévisy, O. Baslé,
R. Marcia de Figueiredo, M. Mauduit,*
J.-M. Campagne* ______ **11830 – 11834**

Copper-Catalyzed Asymmetric Conjugate Addition of Dimethylzinc to Acyl-*N*-methylimidazole Michael Acceptors: a Powerful Synthetic Platform

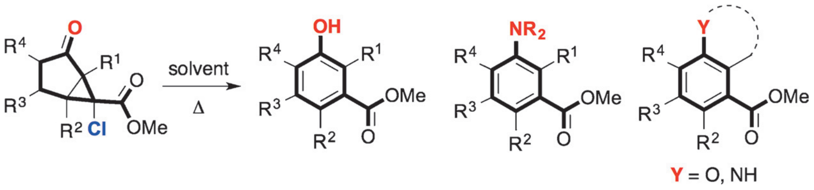


The enantioselective conjugate addition of dimethylzinc to (poly)unsaturated 2-acyl-*N*-methylimidazoles proceeds under Cu catalysis with excellent regio- and enantioselectivities (up to 95% *ee*). The resulting 1,4-adducts can be easily transformed to the corresponding aldehydes, esters, ketones, and amines. This methodology was successfully applied in the synthesis of 1,3-desoxypropionate subunits and natural products.

Arenes

J. Feierfeil, A. Grossmann,
T. Magauer* 11835 – 11838

Ring Opening of Bicyclo[3.1.0]hexan-2-ones: A Versatile Synthetic Platform for the Construction of Substituted Benzoates

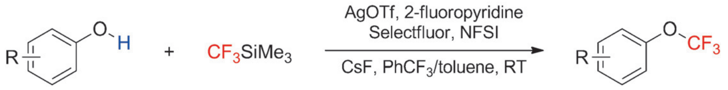


Cracked open: A highly efficient thermal 2π disrotatory ring-opening aromatization sequence of bicyclo[3.1.0]hexan-2-ones is described. The transformation proceeds in sulfolane to give uniquely substituted benzoates. In the presence of either amines or alcohols, formation of substituted anilines or ethers, respectively, is achieved.

Trifluoromethylation

J.-B. Liu, C. Chen, L. Chu, Z.-H. Chen,
X.-H. Xu, F.-L. Qing* 11839 – 11842

Silver-Mediated Oxidative Trifluoromethylation of Phenols: Direct Synthesis of Aryl Trifluoromethyl Ethers



Combining two nucleophiles: The direct oxidative O-trifluoromethylation of phenols with CF_3SiMe_3 provides a general and practical method for the preparation of aryl trifluoromethyl ethers. A wide variety of functional groups are tolerated under these conditions, and the method can also be employed for the late-stage trifluoromethylation of complex pharmaceutically relevant molecules (NFSI = *N*-fluorobenzenesulfonimide).

C–H Activation

S. K. Bose, A. Deißenberger, A. Eichhorn,
P. G. Steel, Z. Lin,
T. B. Marder* 11843 – 11847

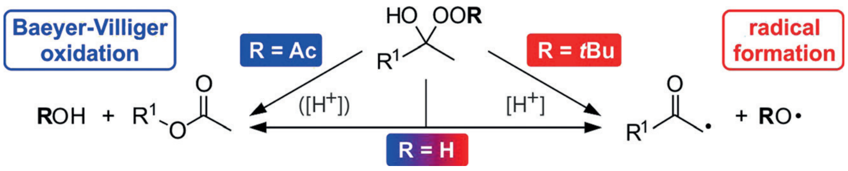
Zinc-Catalyzed Dual C–X and C–H Borylation of Aryl Halides

Two B or not two B: A novel catalytic system based on a Zn^{II}-dtbpy precursor was developed for the preparation of 1,2-diborylarenes. This method represents a new type of catalytic process for diborylation of aryl halides via both C–X and C–H activation.

Reaction Mechanisms

B. Schweitzer-Chaput, T. Kurtén,*
M. Klussmann* 11848 – 11851

Acid-Mediated Formation of Radicals or Baeyer–Villiger Oxidation from Criegee Adducts

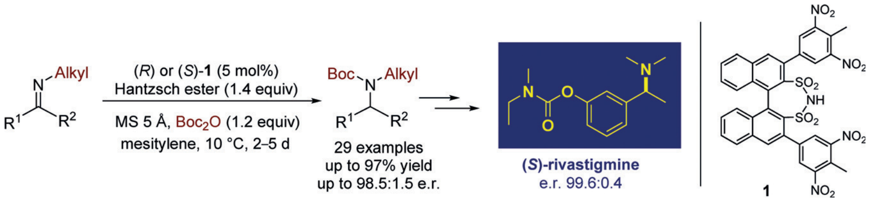


At the crossroads: Criegee adducts of hydroperoxides and ketones are key intermediates in the Baeyer–Villiger oxidation, but they can also generate radicals via formation of alkenyl peroxides. The fate of the Criegee adduct is determined by the electronic nature of the peroxide: peracids favor rearrangement, alkylhydroperoxides favor radical formation. Hydrogen peroxide is equally suitable for both pathways, explaining its poorer performances in the two reactions.

Organocatalysis

V. N. Wakchaure, P. S. J. Kaib,
M. Leutzsch, B. List* —— **11852–11856**

Disulfonimide-Catalyzed Asymmetric Reduction of *N*-Alkyl Imines

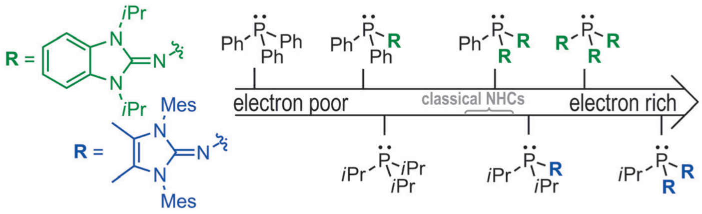


A chiral disulfonimide (DSI)-catalyzed asymmetric reduction of *N*-alkyl imines with Hantzsch esters as a hydrogen source in the presence of Boc_2O was developed. The reaction delivers Boc-protected *N*-alkyl amines with excellent yields and enantioselectivity. The method was successfully applied to the synthesis of the pharmaceuticals (*S*)-Rivastigmine, NPS R-568 Hydrochloride, and (*R*)-Fendiline.

Ligand Design

M. A. Wünsche, P. Mehlmann, T. Witteler,
F. Buß, P. Rathmann,
F. Dielmann* —— **11857–11860**

Imidazolin-2-ylidenaminophosphines as Highly Electron-Rich Ligands for Transition-Metal Catalysts

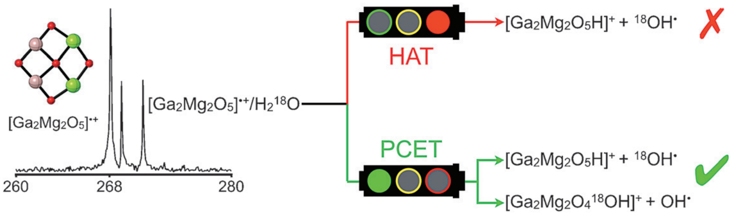


Upgrading phosphines: A conceptually new approach to a family of extremely electron-rich phosphines is based on the use of imidazolin-2-ylidenamino groups directly attached to the phosphorus atom. The steric and electronic properties of the new ligands can be easily varied owing to the general and modular synthesis, which provides new prospects for phosphine ligands in catalysis.

O–H Bond Cleavage

J. Li, S. Zhou, X.-N. Wu, S. Tang,
M. Schlangen,
H. Schwarz* —— **11861–11864**

On the Mechanisms of Hydrogen-Atom Transfer from Water to the Heteronuclear Oxide Cluster $[Ga_2Mg_2O_5]^{\cdot+}$: Remarkable Electronic Structure Effects

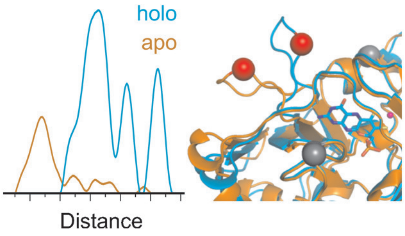


No HAT required: In the $[Ga_2Mg_2O_5]^{\cdot+}/H_2O$ couple, the most favorable pathway corresponds to a proton-coupled electron transfer (PCET) mechanism, while a conventional hydrogen-atom transfer (HAT) mechanism is much more demanding energetically.

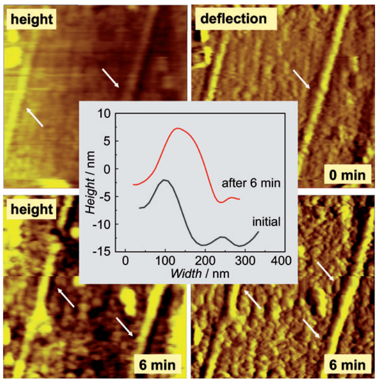
Protein Structure

A. Hahn, C. Engelhard, S. Reschke,
C. Teutloff, R. Bittl, S. Leimkühler,
T. Risse* —— **11865–11869**

Structural Insights into the Incorporation of the Mo Cofactor into Sulfite Oxidase from Site-Directed Spin Labeling



An open and shut case: The structural basis of the incorporation of the Mo cofactor (Moco) into human sulfite oxidase (hSO) was addressed using site-directed spin labeling. Comparative measurements on the holo and apo forms of hSO reveal a highly localized flap-like movement of a short loop, which provides access to the Moco binding pocket. This provides an explanation for the previously observed in vitro reconstitution of apo-hSO.



Semiconductors

A. Lahiri,* N. Borisenko,* M. Olschewski, R. Gustus, J. Zahlbach, F. Endres ______ 11870 – 11874

Electroless Deposition of III–V Semiconductor Nanostructures from Ionic Liquids at Room Temperature

Spontaneous formation of GaSb semiconductor nanostructures is possible using electroless deposition (galvanic displacement) at room temperature in ionic liquids. By changing the cation of the ionic liquid, the reduction rate could be varied leading to different optical properties of the semiconductor. (Picture: AFM images of the electroless displacement of Sb on Ga nanowires from an Sb-containing ionic liquid.)

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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