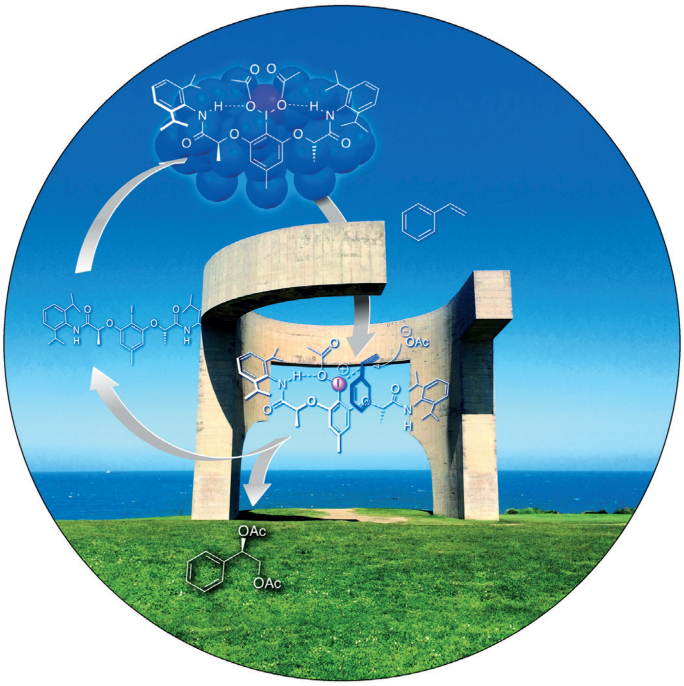
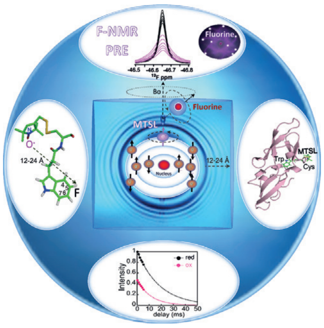
The monumental “Elegy to the Horizon” …

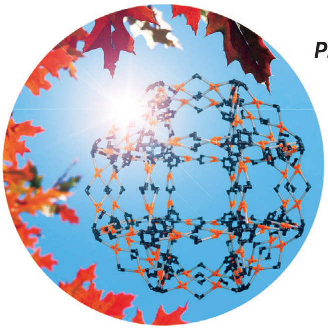


… by the Basque artist Eduardo Chillida oversees the Atlantic coast at the town of Gijón (Asturias, Spain). A similar structural shape is involved in the enantiodiscrimination of alkenes through a chiral iodine(III) catalyst. In their Communication on page 413 ff., K. Muñiz et al. discuss selective hydrogen bonding toward chirally induced supramolecular scaffolds in iodine(III) catalysts and their performance in an intermolecular enantioselective diacetoxylation reaction.

NMR Spectroscopy

^{19}F NMR paramagnetic relaxation enhancements that were evaluated for extracting distance information in a selectively ^{19}F-labeled protein are reported by A. M. Gronenborn and E. Matei in their Communication on page 150 ff.





Photoswitchess

G. H. Clever et al. demonstrate in their Communication on page 445 ff. how light of different wavelengths can be used to reversibly interconvert supramolecular aggregates, as exemplified by a small Pd_3L_6 ring and a 7 nm $Pd_{24}L_{48}$ sphere.

Environmental Chemistry

In their Communication on page 240 ff., M. Spiteller and co-workers unambiguously confirm that synthetic tramadol has indeed contaminated the environment in rural as well as densely populated areas of Northern Cameroon.

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Editorial

From deception to plagiarism, the range of unethical behavior in the publishing practices of scientists is broad. However, scientists should not all be tarred with the same brush. This theme is at the heart of the Editorial that also illuminates some happier events, such as the nomination of new members of the Editorial and International Advisory Boards.

Miscellaneous

Author Profile

"The most exciting thing about my research is that I 'see' molecules.
I can never resist a piece of good chocolate. …"
This and more about Steven De Feyter can be found on page 32.

News


M. Brudermüller


K. Griesar


C. W. Kohlpaintner


J. Cho


P. G. Schultz

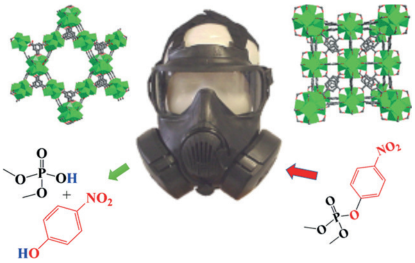

Y. Xie

Books

Highlights

Detoxification of Nerve Agents

Seek and destroy: Filtration schemes and self-detoxifying protective fabrics based on the Zr^{IV}-containing metal—organic frameworks (MOFs) MOF-808 and UiO-66 doped with LiO*t*Bu have been developed that capture and hydrolytically detoxify simulants of nerve agents and mustard gas. Both MOFs function as highly catalytic elements in these applications.



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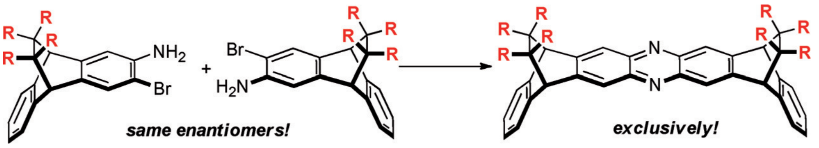
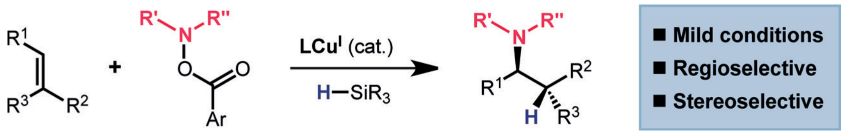
Bent Molecules



Hand in hand: Enantiopure reactants have been used to generate rigid molecular tweezers by Buchwald–Hartwig aminations. These result in the phenazine units curving in only one direction with formation of one product exclusively.

Minireviews

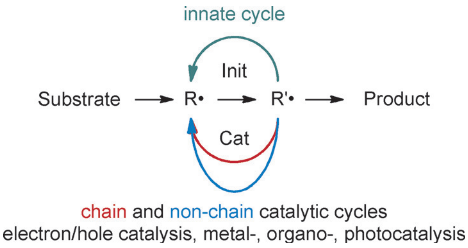
Asymmetric Catalysis



Mild and abundant: CuH-catalyzed hydroamination has recently been developed as a viable method for synthesizing a broad range of chiral aliphatic amines in excellent efficiencies and enantioselectivites. This Minireview highlights advancements made in this area of catalysis along with the precedent that has led to these discoveries.

Reviews

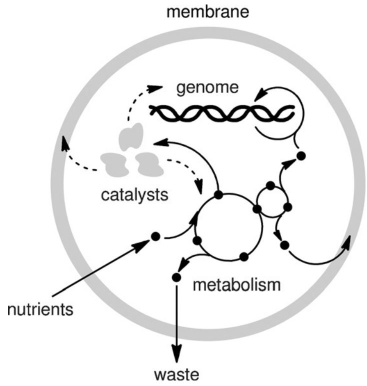
Radical Chemistry



The unique reactivity and selectivity of radicals paired with the possibility to cross between different regimes (radical/ionic/organometallic) results in catalysis of radical reactions playing an important role in organic synthesis. The basic concepts of catalyzed radical reactions are introduced and illustrated with selected examples from classical and recent literature.

Prebiotic Systems Chemistry

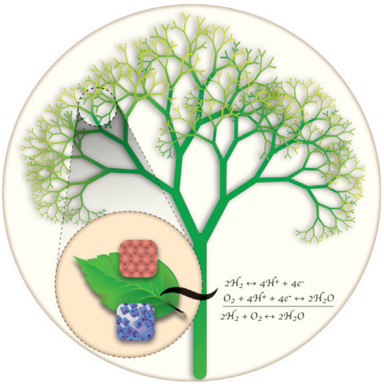
Molecular componentry for all the cellular subsystems can be derived from hydrogen cyanide—“Blausäure”—suggesting life arose “out of the blue”.



Energy Materials

P. Trogadas,* V. Ramani, P. Strasser,
T. F. Fuller, M.-O. Coppens* — **122 – 148**

Hierarchically Structured Nanomaterials for Electrochemical Energy Conversion



Inspired by nature: Hierarchical nanomaterials are highly suitable as electrocatalysts and electrocatalyst supports in electrochemical energy conversion devices. To further improve their design, in-depth research on the effect of materials architecture on reaction and transport kinetics is necessary. Inspiration can be derived from nature, which is full of very effective hierarchical structures.

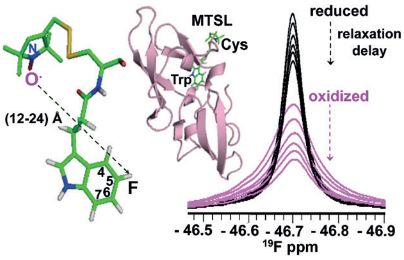
Communications

NMR Spectroscopy

E. Matei, A. M. Gronenborn* — **150 – 154**

^{19}F Paramagnetic Relaxation Enhancement: A Valuable Tool for Distance Measurements in Proteins

Frontispiece

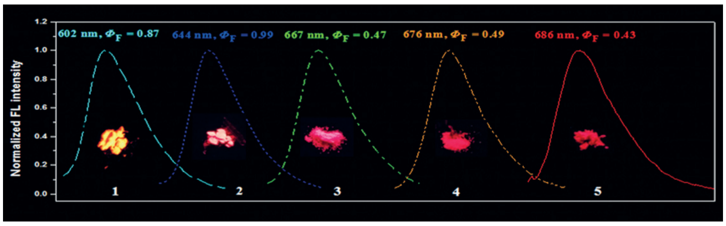


Distance measurement: Fluorine NMR paramagnetic relaxation enhancements (^{19}F-PRE) were evaluated for extracting distance information in a selectively fluorine-labeled protein (MTSL = nitroxide spin label). An initial application is presented for the HIV-inactivating lectin cyanovirin-N. In agreement with theory, based on the gyromagnetic $\gamma(^{19}\mathrm{F})/\gamma(^{1}\mathrm{H})$ ratio, ^{19}F-PRE-based distances can be measured within the range of 12–24 Å.

Fluorescent Probes

H. Lu,* Y. Zheng, X. Zhao, L. Wang, S. Ma,
X. Han, B. Xu, W. Tian,
H. Gao* — **155 – 159**

Highly Efficient Far Red/Near-Infrared Solid Fluorophores: Aggregation-Induced Emission, Intramolecular Charge Transfer, Twisted Molecular Conformation, and Bioimaging Applications

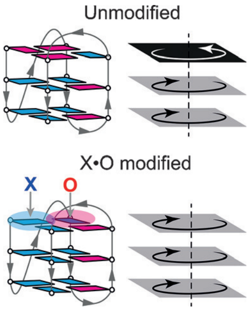


Twisted emissions: Fluorophores with aggregation-induced emission (AIE) in the solid state are reported. The emissions range from the orange to far red/near-infrared (FR/NIR) regions, and the molecules have twisted molecular conformations. The bioimaging performance of the designed fluorophores shows that they have potential as FR/NIR fluorescent probes for biological applications.

G-Quadruplexes

V. V. Cheong, C. J. Lech, B. Heddi,
A. T. Phan* — **160 – 163**

Inverting the G-Tetrad Polarity of a G-Quadruplex by Using Xanthine and 8-Oxoguanine

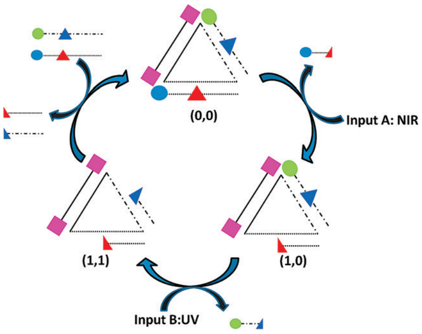


Flip it and reverse it: The judicious incorporation of the guanine analogues xanthine (X) and 8-oxoguanine (O) within a G-quadruplex-forming sequence was shown to reverse the hydrogen-bond polarity of the modified G-tetrad, while maintaining the original folding topology.

DNA Computing

D. Y. Tam, Z. Dai, M. S. Chan, L. S. Liu, M. C. Cheung, F. Bolze,* C. Tin, P. K. Lo* ______ **164 – 168**

A Reversible DNA Logic Gate Platform Operated by One- and Two-Photon Excitations

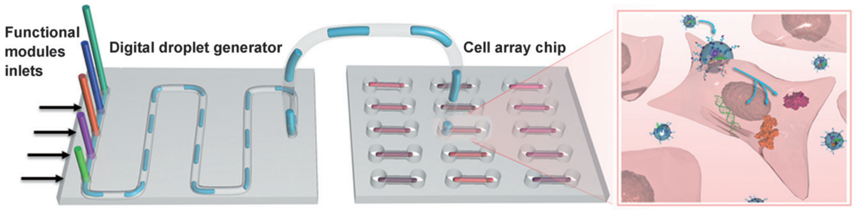


Light logic: A four-part, fluorophore-modified DNA device is designed to operate as an OR logic gate in response to two excitation wavelengths. This device could be reset with excess oligonucleotides, and was shown to be taken up by cultured mammalian cells.

Biomolecular Delivery

Y. Liu, J. Du, J.-s. Choi, K.-J. Chen, S. Hou, M. Yan, W.-Y. Lin, K. S. Chen, T. Ro, G. S. Lipshutz, L. Wu, L. Shi, Y. Lu,* H.-R. Tseng,* H. Wang* ______ **169 – 173**

A High-Throughput Platform for Formulating and Screening Multifunctional Nanoparticles Capable of Simultaneous Delivery of Genes and Transcription Factors

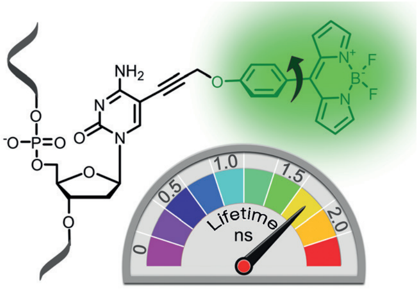


Special delivery: Integration of microfluidic systems with a supramolecular synthetic strategy results in a high-throughput approach to formulating and screening multifunctional supramolecular nanoparticles (see picture). The nanoparticles are self-assembled from a collection of functional modules (proteins, genes, ligands, and a scaffold) and can simultaneously deliver both a gene and transcription factor either in vitro or in vivo.

Fluorescent Probes

D. Dziuba, P. Jurkiewicz, M. Cebecauer, M. Hof,* M. Hocek* ______ **174 – 178**

A Rotational BODIPY Nucleotide: An Environment-Sensitive Fluorescence-Lifetime Probe for DNA Interactions and Applications in Live-Cell Microscopy



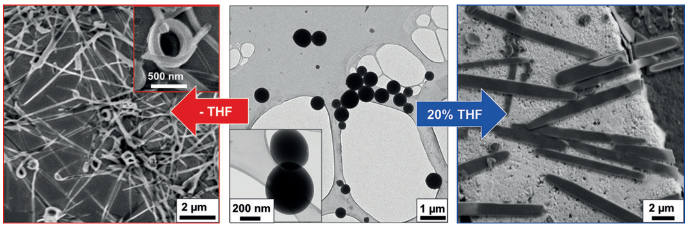
Rotational probe: A probe comprising a nucleoside linked to a meso-substituted BODIPY fluorescent molecular rotor (see picture) can be used to sense changes in the DNA microenvironment both in vitro and in living cells. Changes in the fluorescence lifetime of the probe allow detection of interactions with DNA-binding proteins or lipids.

Inside Cover

Crystallization

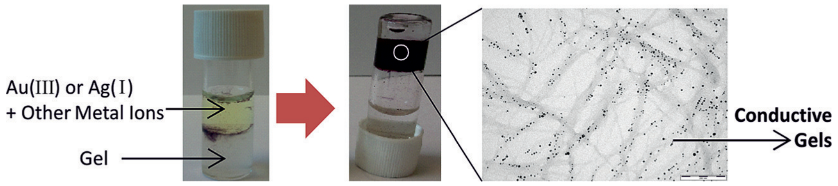
C. Shahar, S. Dutta, H. Weissman, L. J. W. Shimon, H. Ott, B. Rybtchinski* ______ **179 – 182**

Precrystalline Aggregates Enable Control over Organic Crystallization in Solution



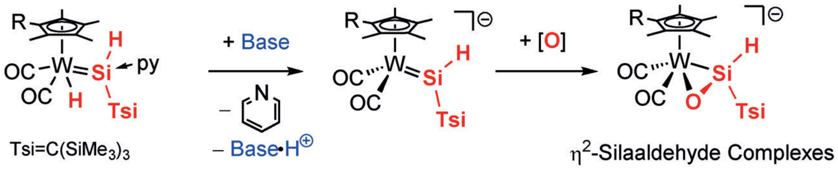
Order evolution: Initially formed amorphous structures are important precursors in organic crystallization. One can manipulate the amorphous precrystalline phase to hinder crystallization or control its outcome. These findings introduce a conceptually new strategy to control crystallization by precrystalline state manipulation.

Functional Gels



From waste to wealth: Hydrazide-functionalized hydrogels extract and reduce precious metal waste into nanoparticles, and thereby generate conductive gel-phase materials with potential electronic applications.

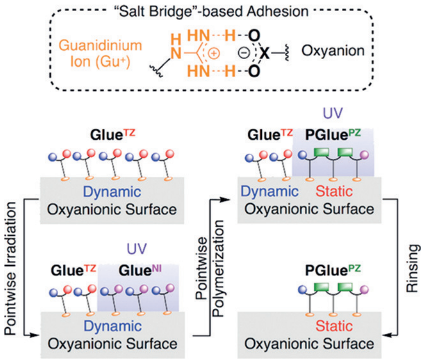
Silylene Complexes



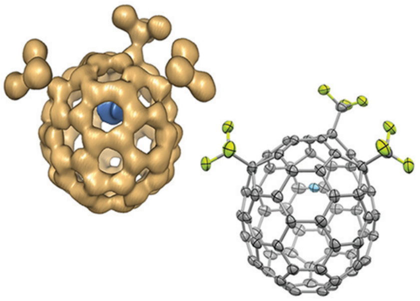
Closing the circle: Anionic silylene complexes, prepared by proton abstraction from pyridine-stabilized hydrido(hydrosilylene) compounds, were oxidized using pyridine-*N*-oxide to form η^2-silaaldehyde complexes. Formation of a W-Si-O three-membered ring was confirmed by X-ray crystallography.

Adhesive Surfaces

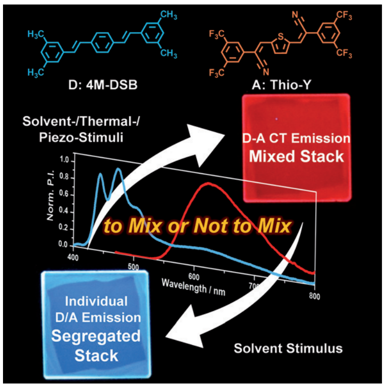
Stuck on glue: Novel photoinduced bioorthogonal polymerization of a guanidinium ion (Gu^+) appended water-soluble monomer was developed. It allows, by use of a focused beam of UV light, spatiotemporal functionalization of oxyanionic substrates, such as DNA and living cells as well as silica and latex nanoparticles, with the fluorescent molecular glue $PGlue^{PZ}$.



Metallofullerenes

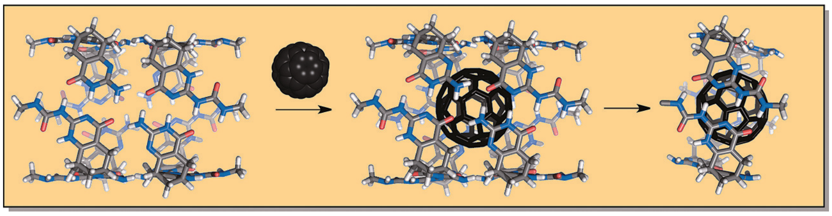


The missing link: The molecular structure of a missing metallofullerene La@C_{70} was determined for the first time through in situ trifluoromethylation of the fullerene cage, followed by single-crystal X-ray diffraction. La@C_{70} is greatly stabilized as a consequence of trifluoromethylation-induced bandgap enlargement.



To mix or not to mix: A donor–acceptor (D-A) charge-transfer (CT) crystalline film was designed to realize stimuli-responsive reversible fluorescence switching media. Owing to the loosely packed CT state, reorganization between the red-emissive mixed CT phase and blue-emissive demixed self-sorted phase can be demonstrated by external triggers such as solvent, thermal, and piezomechanical stimuli.

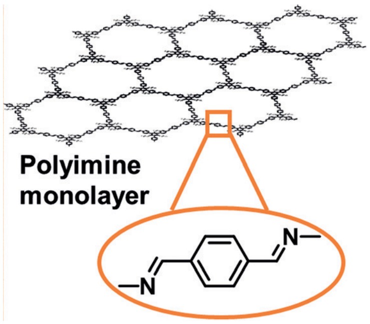
Fluorescent Crystals



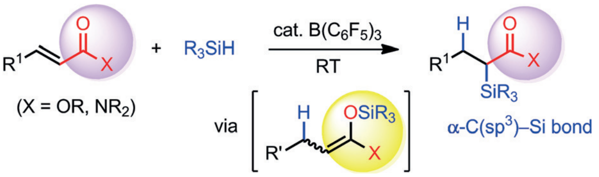
Be my guest: An octameric supramolecular tube was assembled from identical small bicyclic building blocks by means of selective heterodimerization between isocytosine and ureidopyrimidinone hydrogen-bonding units. Upon treatment with C_{60}, the hydrogen-bonding mode is switched, leading to rearrangement of the tube into a tetrameric inclusion complex.

Supramolecular Chemistry

On the edge: A large, two-dimensional, covalently bound organic monolayer was synthesized through dynamic imine chemistry at the air/water interface. The imine-linked chemical structure of the aromatic monolayer was characterized by tip-enhanced Raman spectroscopy (TERS) and further supported by density functional theory (DFT) simulations.



Monolayers



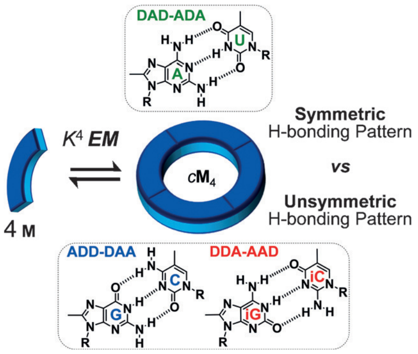
Two steps: $B(C_6F_5)_3$-catalyzed hydrosilylation of α,β-unsaturated esters and amides affords synthetically valuable α-silyl carbonyl products. The α-silylation occurs chemoselectively, thus leaving the labile carbonyl groups intact. This reaction proceeds by two steps: fast 1,4-hydrosilylation of conjugated carbonyls and then slow silyl group migration of a silyl ether intermediate.

Hydrosilylation

Self-Assembly

C. Montoro-García, J. Camacho-García, A. M. López-Pérez, M. J. Mayoral, N. Bilbao, D. González-Rodríguez* ______ **223 – 227**

Role of the Symmetry of Multipoint Hydrogen Bonding on Chelate Cooperativity in Supramolecular Macrocyclization Processes



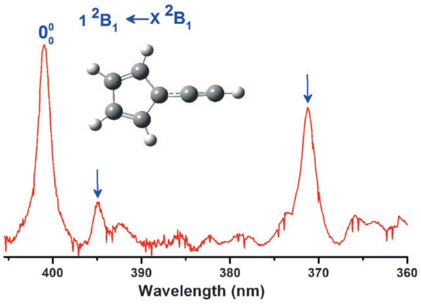
Symmetry matters: Analysis of the intrinsic chelate effect that multipoint H-bonding patterns exert on the overall energy of dinucleoside cyclic systems showed that the magnitude of the effective molarity (*EM*) is regulated by the symmetry of the H-bonding pattern. The *EM* value was about three orders of magnitude lower for the symmetric DAD–ADA pattern than for the unsymmetric ADD–DAA and DDA–AAD patterns (see picture).

Electronic Spectroscopy

A. Chakraborty, J. Fulara, J. P. Maier* ______ **228 – 231**

The Electronic Spectrum of the Fulvenallenyl Radical

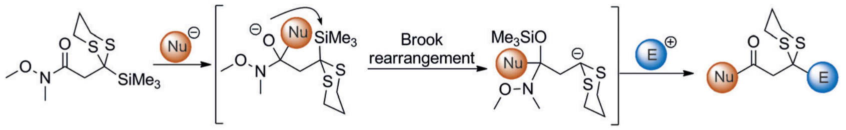
Finding proof: The fulvenallenyl radical, a key intermediate in the formation of polycyclic aromatic hydrocarbons, was produced in 6 K neon matrices after mass-selective deposition of $C_7H_5^-$ and $C_7H_5^+$ generated from organic precursors in a hot cathode ion source. On the basis of electronic absorption spectra and calculated excitation energies, the key absorption system (blue arrows) is assigned to the $1\,^2B_1 \leftarrow X\,^2B_1$ transition of the radical.



Brook Rearrangement

M. Farrell, B. Melillo, A. B. Smith III* ______ **232 – 235**

Type II Anion Relay Chemistry: Exploiting Bifunctional Weinreb Amide Linchpins for the One-Pot Synthesis of Differentiated 1,3-Diketones, Pyrans, and Spiroketals

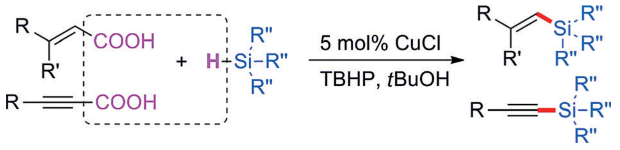


A highly effective bifunctional linchpin for type II anion relay chemistry has been developed. The mechanistically novel negative-charge migration that comprises a Brook rearrangement is initiated by a stabilized tetrahedral intermediate that is generated by nucleophilic addition to a Weinreb amide rather than by a simple, epoxide-derived oxyanion.

Radical Reactions

L. Zhang, Z. Hang, Z.-Q. Liu* ______ **236 – 239**

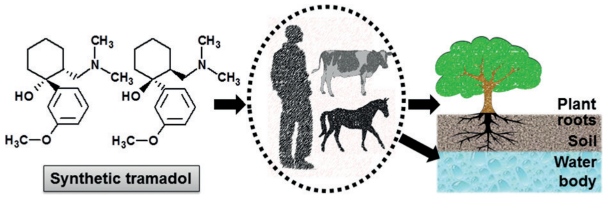
A Free-Radical-Promoted Stereospecific Decarboxylative Silylation of α,β-Unsaturated Acids with Silanes



A radical transformation: A stereospecific decarboxylative silylation of acrylic and propiolic acids with silanes was developed. This method provides an efficient and convenient approach to various synthetically useful alkenyl and alkynyl organosilicon compounds through the reaction of α,β-unsaturated acids with silanes. Spin-trapping and EPR experiments support a radical addition/elimination process.

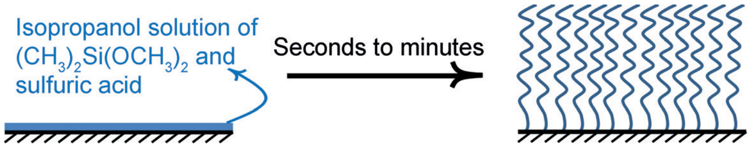
Environmental Chemistry

Back Cover



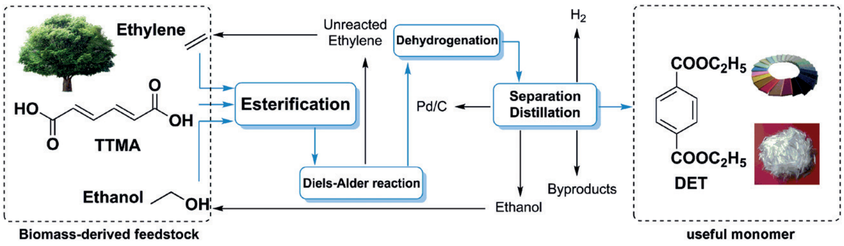
The presence of tramadol in roots of *Sarcocephalus latifolius* trees and several other plant species as well as its occurrence in the soil and the surface and ground water in Northern Cameroon raised the question whether these traces are of natural or synthetic origin. Various measurements, for example, by accelerator mass spectrometry to determine the ^{14}C content, unambiguously confirm that synthetic tramadol has contaminated the environment.

Surface Chemistry



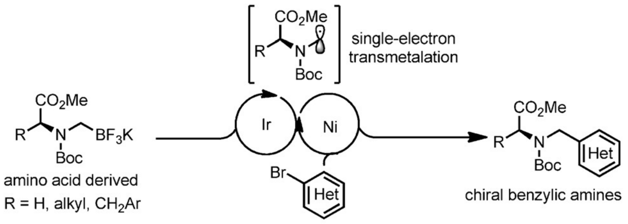
Omniphobic surfaces that are stable under pressure and durable at elevated temperatures were obtained by acid-catalyzed graft polycondensation of dimethyldimethoxysilane. The slippery omniphobic covalently attached liquid (SOCAL) surfaces show extremely low contact angle hysteresis (≤1°) and low sliding angles for liquids with surface tensions from 78.2 to 18.4 mN m^{-1}.

Biomass Conversion



Diethyl terephthalate is obtained from biomass-derived *trans,trans*-muconic acid through a cascade process combining esterification, Diels–Alder cycloaddition, and dehydrogenation. The esterification reaction significantly improves the solubility of the diester product in ethanol and promotes the Diels–Alder reaction.

Cross-Coupling

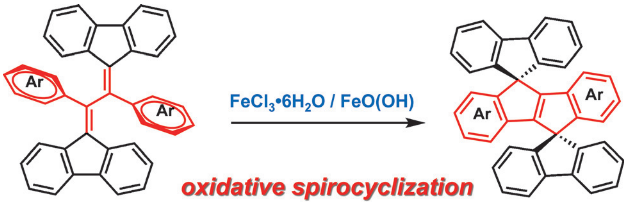


Making light of it: A novel dual catalytic route to enantiopure benzylic amines is outlined, and it takes advantage of photoredox catalysis in conjunction with nickel-catalyzed cross-coupling. The starting materials are robust organotrifluoroborates that can engage, with an expanded range of densely functionalized aryl- and heteroaryl halides, in the title reaction.

Conjugation

J. Zhao, Z. Xu, K. Oniwa, N. Asao,
Y. Yamamoto, T. Jin* ________ 259 – 263

FeCl$_3$-Mediated Oxidative Spirocyclization of Difluorenylidene Diarylethanes Leading to Dispiro[fluorene-9,5′-indeno[2,1-*a*]-indene-10′,9′′-fluorene]s

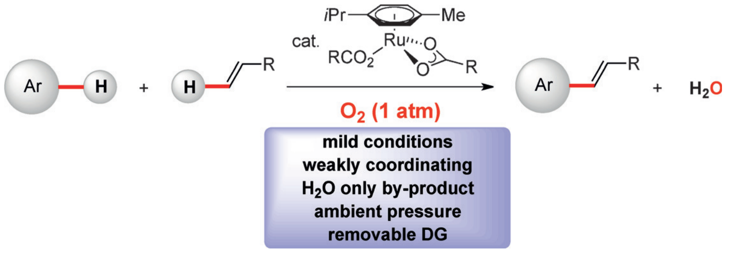


Ironed out: The title reaction has been developed for the construction of a new class of di-spirolinked π-conjugated molecules, dispiro[fluorene-9,5′-indeno[2,1-*a*]indene-10′,9′′-fluorene]s. The highest fluorescence quantum yield of the dispirocycle was up to 0.94 in solution.

C–H Activation

A. Bechtoldt, C. Tirler, K. Raghuvanshi,
S. Warratz, C. Kornhaaß,
L. Ackermann* ________ 264 – 267

Ruthenium Oxidase Catalysis for Site-Selective C–H Alkenylations with Ambient O$_2$ as the Sole Oxidant

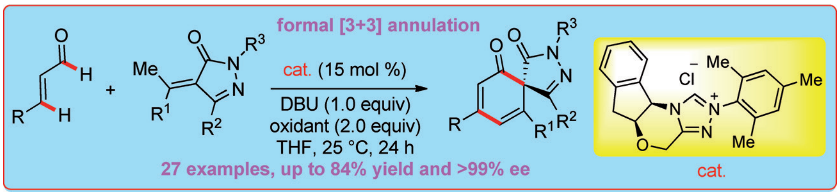


O$_2$ can do: Ruthenium(II) oxidase catalysis by direct dioxygen-coupled turnover is used for efficient twofold C–H functionalization reactions under exceedingly mild reaction conditions. The versatile ruthenium(II) carboxylate catalyst featured a broad substrate scope and an excellent positional selectivity.

Organocatalysis

S. R. Yetra, S. Mondal, S. Mukherjee,
R. G. Gonnade, A. T. Biju* ____ 268 – 272

Enantioselective Synthesis of Spirocyclohexadienones by NHC-Catalyzed Formal [3+3] Annulation Reaction of Enals

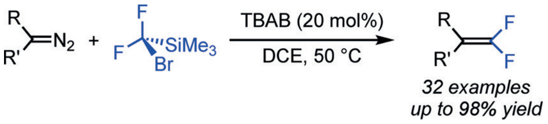


Spiral-bound: An N-heterocyclic carbene (NHC) catalyzed formal [3+3] annulation reaction of enals with pyrazolinones for the enantioselective synthesis of spirocyclohexadienones is reported. The NHC-bound chiral α,β-unsaturated acyl azolium undergoes interception with the dienolate/enolate intermediates generated in tandem from pyrazolinones to afford spirocompounds in moderate to good yields and with excellent *ee* values.

Difluorocarbene

Z. Zhang, W. Yu, C. Wu, C. Wang, Y. Zhang,
J. Wang* ________ 273 – 277

Reaction of Diazo Compounds with Difluorocarbene: An Efficient Approach towards 1,1-Difluoroolefins

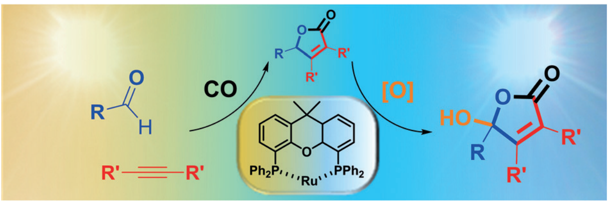


Formal carbene dimerization: The difluoromethylenation of diazo compounds was achieved under mild conditions with TMSCF$_2$Br as the difluoromethylene source and tetrabutylammonium bromide (TBAB) as the initiator. The chemoselective formal carbene dimerization is achieved owing to the electronic properties and the relative stability of the difluorocarbene intermediate.

Heterocycles

H. Miura, K. Takeuchi,
T. Shishido* ________ **278 – 282**

Intermolecular [2+2+1] Carbonylative Cycloaddition of Aldehydes with Alkynes, and Subsequent Oxidation to γ-Hydroxybutenolides by a Supported Ruthenium Catalyst

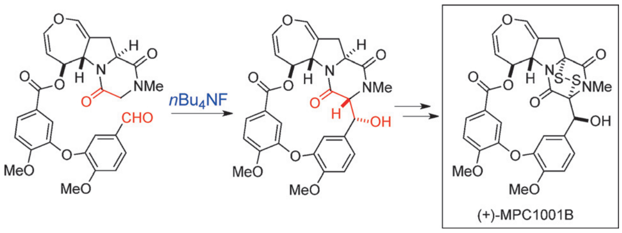


Gaining support: The title reaction is achieved using a supported ruthenium catalyst. The ceria-supported ruthenium catalyst promotes the reaction efficiently even with an ambient pressure of CO, thus giving the corresponding γ-hydroxybutenolide derivatives in good to high yields. Moreover, this catalyst can be reused with no loss of activities.

Alkaloid Synthesis

T. Kurogi, S. Okaya, H. Fujiwara, K. Okano,
H. Tokuyama* ________ **283 – 287**

Total Synthesis of (+)-MPC1001B

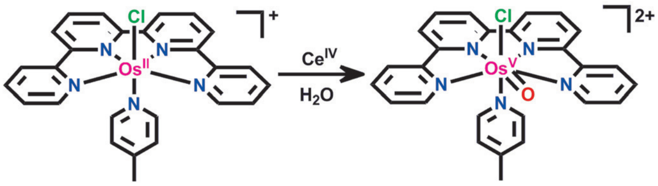


Going round in circles: The first total synthesis of an epidithiodiketopiperazine alkaloid, (+)-MPC1001B, was accomplished through a sequence involving a TBAF-mediated intramolecular aldol reaction to form the 15-membered macrolactone ring, and construction of an epidithiodiketopiperazine through a stepwise sulfenylation reaction involving a novel trityl trisulfide (TrSSS) group transfer.

C–H Activation

Y. Liu, S. M. Ng, W. W. Y. Lam, S. M. Yiu,
T. C. Lau* ________ **288 – 291**

A Highly Reactive Seven-Coordinate Osmium(V) Oxo Complex: $[\mathrm{Os^{V}(O)(qpy)(pic)Cl}]^{2+}$



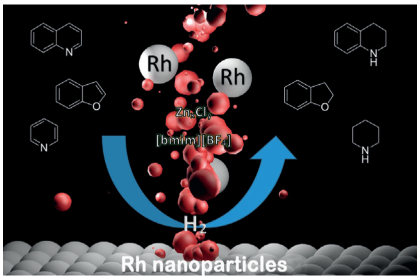
The magnificent seven: Oxidation of $[\mathrm{Os^{II}(qpy)(pic)Cl}]^{+}$ with cerium(IV) generates the first seven-coordinate Group 8 oxo species, $[\mathrm{Os^{V}(O)(qpy)(pic)Cl}]^{2+}$, which can abstract an H atom from alkylarenes with C–H bond dissociation energies as high as 90 $\mathrm{kcal\,mol^{-1}}$. The structure elucidation is also discussed. pic = 4-picoline, qpy = 2,2′:6′,2′′:6′′,2′′′-quaterpyridine.

Nanoparticle Catalysis

A. Karakulina, A. Gopakumar, İ. Akçok,
B. L. Roulier, T. LaGrange, S. A. Katsyuba,
S. Das,* P. J. Dyson* ________ **292 – 296**

A Rhodium Nanoparticle–Lewis Acidic Ionic Liquid Catalyst for the Chemoselective Reduction of Heteroarenes

A rhodium nanoparticle catalyst immobilized in a Lewis acidic ionic liquid is described. The combined system catalyzes the hydrogenation of quinolines, pyridines, benzofurans, and furan to access the corresponding heterocycles.

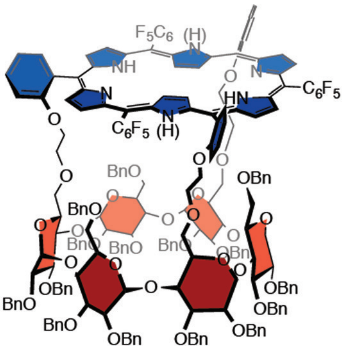


Supramolecular Chemistry

M. Ménand,* M. Sollogoub, B. Boitrel, S. Le Gac* ______ 297 – 301

Hexaphyrin–Cyclodextrin Hybrids: A Nest for Switchable Aromaticity, Asymmetric Confinement, and Isomorphic Fluxionality

In a state of flux: When an α-cyclodextrin was capped covalently with a hexaphyrin(1.1.1.1.1.1) derivative (see structure), the 26 and 28 π-electron oxidation states of the planar hexaphyrin unit were interconvertible, thus affording a rare switchable aromatic–antiaromatic system. The hexaphyrin cap with a rectangular conformation appeared to rotate above the cyclodextrin through a short-side-to-long-side shape-shifting mechanism.

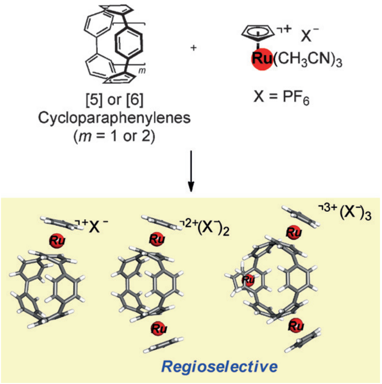


Arene–Ruthenium Complexes

E. Kayahara, V. K. Patel, A. Mercier, E. P. Kündig, S. Yamago* ______ 302 – 306

Regioselective Synthesis and Characterization of Multinuclear Convex-Bound Ruthenium-[*n*]Cycloparaphenylene (*n* = 5 and 6) Complexes

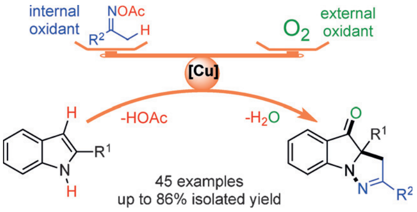
Round and around: Mono- and multinuclear complexes of ruthenium and [*n*]cycloparaphenylene (CPP, *n* = 5 and 6) were synthesized in excellent yield through ligand exchange of the cationic complex $[(Cp)Ru(CH_3CN)_3](PF_6)$ with CPP. In the multinuclear complexes, ruthenium selectively coordinated to alternate paraphenylene units. Single-crystal X-ray analysis revealed the Ru was coordinated with η^6-hapticity on the convex surface of CPP.



Indole Oxygenation

H. Huang,* J. Cai, X. Ji, F. Xiao, Y. Chen, G.-J. Deng* ______ 307 – 311

Internal Oxidant-Triggered Aerobic Oxygenation and Cyclization of Indoles under Copper Catalysis



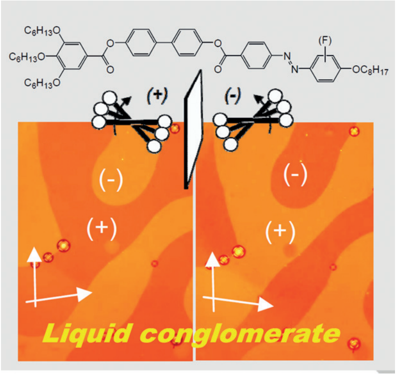
A concise synthesis of pyrazolo[1,5-a]-indole derivatives by copper-catalyzed aerobic oxygenation and cyclization of indoles with oxime acetates is described. This method provides an elegant route for N-1, C-2, and C-3 trifunctionalization of indoles in one pot.

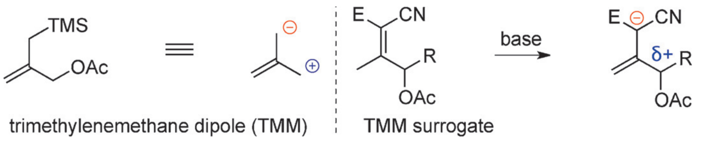
Chirality

M. Alaasar,* M. Prehm, Y. Cao, F. Liu,* C. Tschierske* ______ 312 – 316

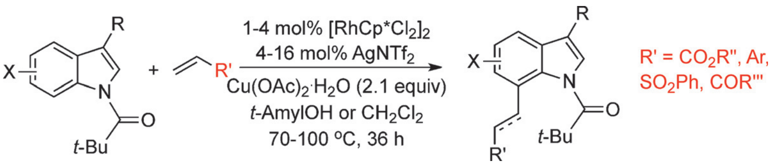
Spontaneous Mirror-Symmetry Breaking in Isotropic Liquid Phases of Photoisomerizable Achiral Molecules

Let's twist again: Chirality synchronization leads to spontaneous conglomerate formation of domains with opposite chirality in isotropic liquids of specifically designed achiral azobenzene-based molecules. Fluorination of the aromatic core was a powerful tool to tailor the temperature range of these spontaneously chiral liquids. The liquid conglomerates occur in a new phase sequence adjacent to 3D tetragonal mesophases.

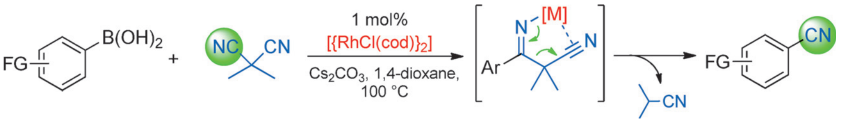




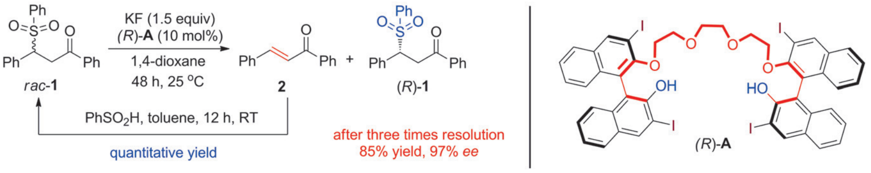
As good as the real thing: Acyloxy Knoevenagel adducts derived from ketones and malonic acid derivatives served as trimethylenemethane dipole surrogates in a sequence involving selective γ-deprotonation/α-alkylation and palladium(0)-catalyzed allylic alkylation (see scheme). As well as a three-component 1,3-difunctionalization of Knoevenagel adducts, a unique "branched-selective" allylic alkylation was developed.



Seven at one blow: Direct C–H functionalization at the 7-position of *N*-pivalylindoles was promoted efficiently by a rhodium catalyst without the need to protect or block the 2-position. Alkenylation products were formed with acrylate, styrene, and vinyl phenyl sulfone coupling partners, whereas alkylation products were obtained with α,β-unsaturated ketones (see scheme).



Hot DMMN: A carbon-bound electrophilic CN source, dimethylmalononitrile (DMMN), undergoes transnitrilation with aryl boronic acids. Compared to other cyanating reagents, DMMN is stable, safe, and commercially available. This novel rhodium-catalyzed process tolerates various functional groups, thus making it a practical method to access aryl nitriles.

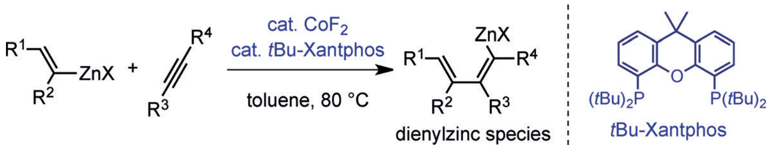


Paired off: The title reaction leads to effective resolution of a wide range of β-sulfonyl ketones (**1**) with high stereoselectivity. Key to the success of this process is the favorable secondary interactions of the catalyst with the Lewis basic groups on the substrate. The enone product can be easily converted into the racemic starting material and allows effective recycling, and thus isolation of β-sulfonyl ketones in high yield and excellent enantioselectivity.

Homogeneous Catalysis

J. Wu, N. Yoshikai* ______ 336–340

Cobalt-Catalyzed Alkenylzincation of Unfunctionalized Alkynes

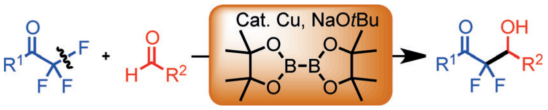


Just diene to share: carbometalation reactions of unfunctionalized alkynes using alkenylmetal reagents remain largely unexplored. A cobalt/diphosphine catalyst is reported which promotes efficient and stereoselective addition of alkenylzinc reagents to unfunctionalized internal alkynes. The resulting dienylzinc species serve as versatile intermediates for further synthetic transformations.

Aldol Reaction

R. Doi, M. Ohashi, S. Ogoshi* 341–344

Copper-Catalyzed Reaction of Trifluoromethylketones with Aldehydes via a Copper Difluoroenolate

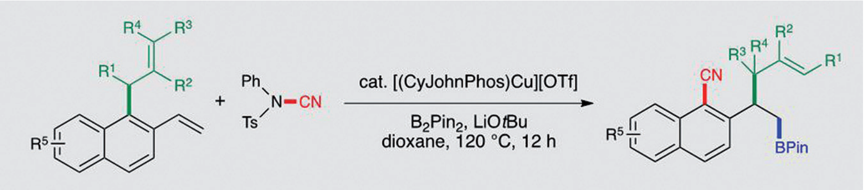


CuB's work: The title reaction affords difluoromethylene compounds in the presence of diboron and NaO*t*Bu. Mechanistic studies show unique reactivity and equilibrium of a key intermediate, copper difluoroenolate, generated by β-fluoride elimination after 1,2-addition of boryl copper species to trifluoromethylketone.

Sigmatropic Rearrangement

Y. Yang* ______ 345–349

Regio- and Stereospecific 1,3-Allyl Group Transfer Triggered by a Copper-Catalyzed Borylation/*ortho*-Cyanation Cascade

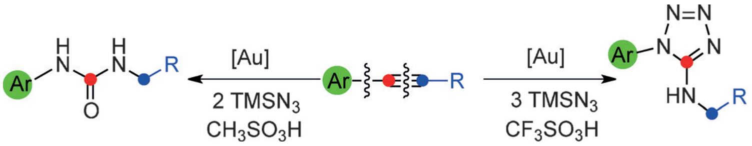


Cut and stitch: A regio- and stereospecific 1,3-allyl group transposition initiated by a copper-catalyzed borylation/dearomative *ortho*-cyanation cascade was developed. This method provides rapid access to a variety of highly functionalized building blocks that can be easily transformed into useful molecular architectures.

C—C Bond Cleavage

C. Qin, Y. Su, T. Shen, X. Shi,*
N. Jiao* ______ 350–354

Splitting a Substrate into Three Parts: Gold-Catalyzed Nitrogenation of Alkynes by C—C and C≡C Bond Cleavage

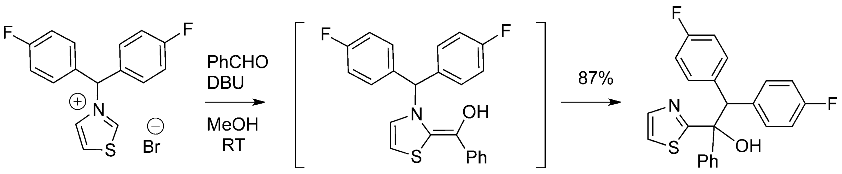


Split and reassemble: Au-catalyzed C—C and C≡C bond cleavage of alkynes for the direct synthesis of amino tetrazoles and carbamides has been achieved. The chemoselectivity can be easily switched by the selection of the acid additives.

Breslow Intermediates

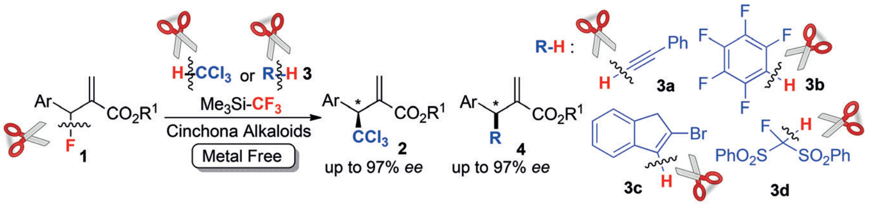
S. Alwarsh, Y. Xu, S. Y. Qian,
M. C. McIntosh* ______ 355–358

Radical [1,3] Rearrangements of Breslow Intermediates



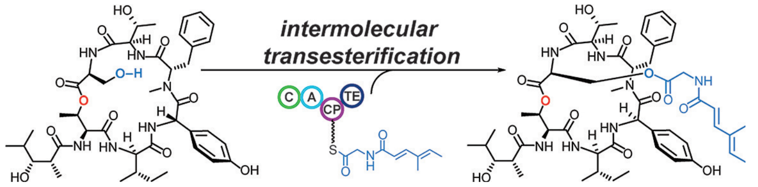
Taking radical action: The reaction of azolium salts having radical-stabilizing N substituents with aromatic aldehydes affords products of formal [1,3] rearrangement instead of benzoin condensation. The surprising instability of the Breslow intermediate leads to N—C bond homolysis at temperatures as low as room temperature.

Organocatalysis



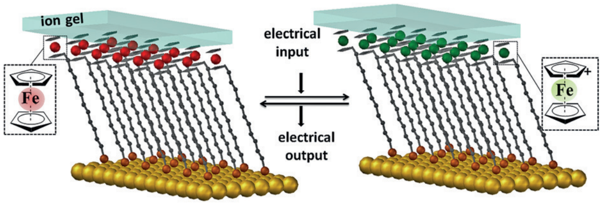
Metal-free trichloromethylation: Silicon-assisted C–F bond activation by a Ruppert-Prakash reagent and direct activation of $HCCl_3$ by a trifluoromethyl (CF_3) carbanion exchange process realized the direct asymmetric trichloromethylation at stereogenic allylic positions, without any help from transition–metal catalysis.

Biosynthesis



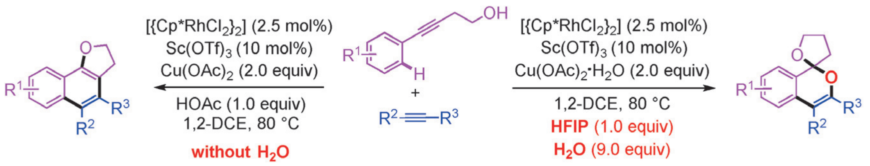
Uncovering the biosynthesis of salinamide A has illuminated a type I thioesterase that plays a pivotal role in the installation of an acylglycine handle across the relatively simple hexadepsipeptide core in an unprecedented intermolecular peptidyl transesterification. The enzyme catalyzes the transfer of an acylated glycine from a carrier protein (CP) to a serine hydroxy group within the off-loaded non-ribosomal peptide product.

Molecular Switches



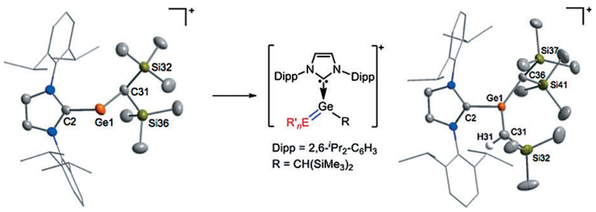
An ionic gel is used as the electrolyte medium in an unprecedented electrochemically switchable solid-state device that is based on a single molecular layer. Furthermore, these devices can be written and erased as well as read by electrochemical impedance spectroscopy.

Cyclization Reactions



You call the tune: Two tunable cascade reactions of alkynols with alkynes were developed by combining $Sc(OTf)_3$ and rhodium catalysis. The same starting materials could be transformed selectively through cycloisomerization and C–H activation into two types of products: 2,3-dihydronaphtho[1,2-*b*]furans and 4,5-dihydro-3*H*-spiro[furan-2,1′-isochromene] derivatives (see scheme).

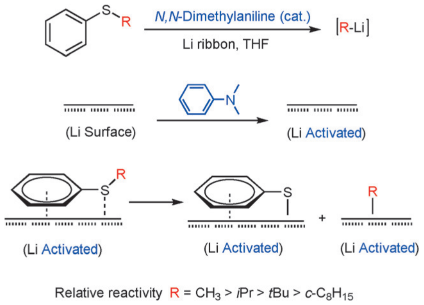
Germanium Double Bonds



Positive germanium: The synthesis of an acyclic dicoordinated germanium(II) cation is reported. This species is shown to undergo oxidative addition, resulting in cations containing Ge=C and Ge=N double bonds.

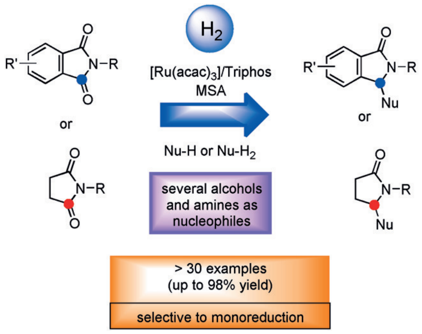
Reaction Mechanisms

Surface deep: The reductive lithiation of phenyl thioethers proceeds by either preformed aromatic radical anions or by lithium metal and an aromatic electron-transfer catalyst. These two methods are fundamentally different: reductions with radical anions occur in solution, whereas the catalytic reaction occurs on the surface of lithium, which is constantly reactivated by the catalyst. A catalytic amount of *N*,*N*-dimethylaniline (DMA) and Li ribbon can achieve reductive lithiation.

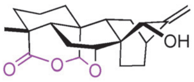


Reduction Reactions

Valorization of imides: Novel catalytic hydrogenations of imides proceed in high yields under comparably mild reaction conditions (see scheme). In the case of aryl-ring-substituted derivatives, notable regioselective transformations are achieved for the first time.

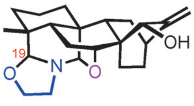


Total Synthesis

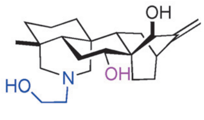


spiramilactone B

spiraminol

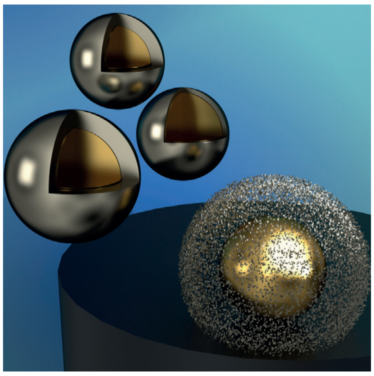


spiramine C, 19*S*
spiramine D, 19*R*



dihydroajaconine

From start to finish: The total syntheses of the architecturally complex atisane-type diterpenes and biogenetically related atisine-type diterpenoid alkaloids (±)-spiramilactone B, (±)-spiraminol, (±)-dihydroajaconine, and (±)-spiramines C and D are reported. The synthetic method includes a late-stage biomimetic transformation of spiramilactone B.



Getting to the core of the matter: The electrochemical characterization of core–shell nanoparticles is demonstrated, providing a quantitative approach to measure the core and shell dimensions on an individual nanoparticle basis. Excellent agreement was obtained between this method and electron microscopy analysis, thereby establishing this as a powerful characterization tool for core–shell nanoparticles.

Electrochemistry

L. R. Holt, B. J. Plowman, N. P. Young, K. Tschulik,* R. G. Compton* **397 – 400**

The Electrochemical Characterization of Single Core–Shell Nanoparticles

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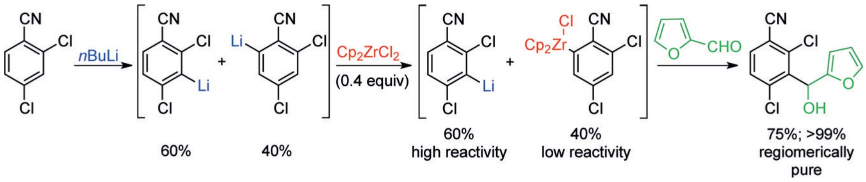

Zirconium is the choice: Mixtures of regioisomeric aryllithium compounds can now be selectively transmetalated with Cp_2ZrCl_2 based on steric effects. Since the most sterically encumbered lithium species is not transmetalated, it can react with various electrophiles.

Transmetalation

A. Castelló-Micó, S. A. Herbert, T. León, T. Bein, P. Knochel* **401 – 404**

Functionalizations of Mixtures of Regioisomeric Aryllithium Compounds by Selective Trapping with Dichlorozirconocene

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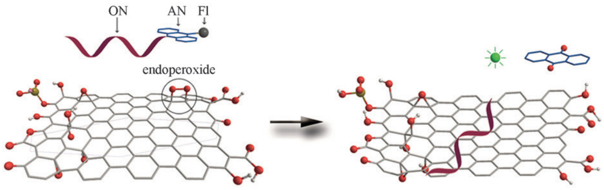

Guilty as charged: The biomedicinal application of graphene oxide (GO) is limited by its cytotoxicity and mutagenicity. To determine which chemical fragments of GO are responsible for this toxicity, GOs containing variable redox-active groups on the surface were generated and compared. The results reveal that endoperoxides play a decisive role in GO-induced oxidative stress.

Graphene Oxide

H. Pieper, S. Chercheja, S. Eigler, C. E. Halbig, M. R. Filipovic, A. Mokhir* **405 – 407**

Endoperoxides Revealed as Origin of the Toxicity of Graphene Oxide

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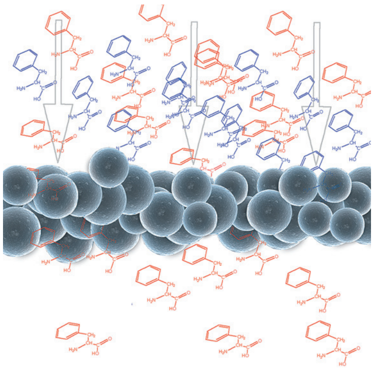


Enantioselective carbon: Enantioselective nanoporous carbon materials were synthesized from chiral ionic liquids and characterized by CD spectroscopy, isothermal titration calorimetry, and chronoamperometry. This approach provides access to a new type of chiral mesoporous materials as well as insights into the properties of the products.

Carbon Materials

I. Fuchs, N. Fechler, M. Antonietti, Y. Mastai* **408 – 412**

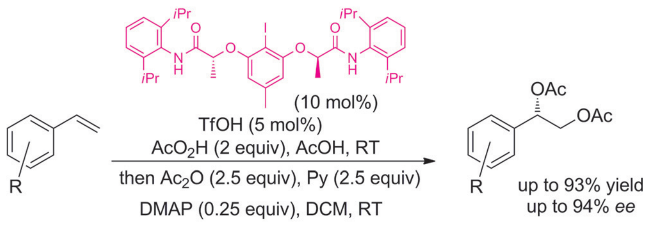
Enantioselective Nanoporous Carbon Based on Chiral Ionic Liquids

Oxidation

S. Haubenreisser, T. H. Wöste,
C. Martínez, K. Ishihara,
K. Muñiz* ______ 413 – 417

Structurally Defined Molecular Hypervalent Iodine Catalysts for Intermolecular Enantioselective Reactions

Front Cover

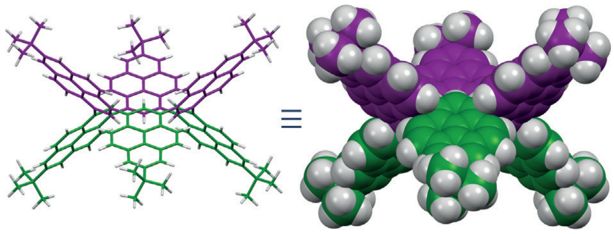


The "I"s have it: The enantioselective vicinal dioxygenation of styrene derivatives under mild conditions is catalyzed by chiral hypervalent iodine(III) compounds which are formed in situ from aryl iodines. Through hydrogen bonds, the *ortho*-substituents give rise to a chiral helical environment around the iodine(III) center and thus enable high asymmetric induction.

Graphene-like Hydrocarbons

D. Lorbach, A. Keerthi,
T. M. Figueira-Duarte, M. Baumgarten,
M. Wagner, K. Müllen* ______ 418 – 421

Cyclization of Pyrene Oligomers: Cyclohexa-1,3-pyrenylene

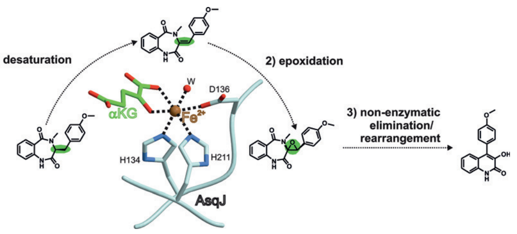


A double cone: A synthetic route has been developed to give a double-cone shaped six-membered pyrene macrocycle, thus extending the aromatic system of the cyclohexa-*m*-phenylene.

Metalloenzymes

A. Bräuer, P. Beck, L. Hintermann,*
M. Groll* ______ 422 – 426

Structure of the Dioxygenase AsqJ: Mechanistic Insights into a One-Pot Multistep Quinolone Antibiotic Biosynthesis

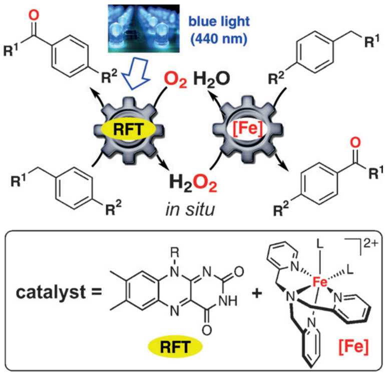


Multitalented: Crystallographic analysis gave detailed structural insight into the complex one-pot multistep reaction catalyzed by the Fe^{II}/α-ketoglutarate-dependent dioxygenase AsqJ. A ferryl-induced desaturation reaction and epoxidation is followed by a non-enzymatic elimination/rearrangement to give the quinolone alkaloid 4′-methoxyviridicatin.

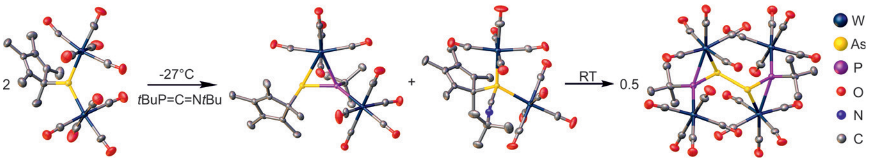
Photocatalysis

B. Mühldorf, R. Wolf* ______ 427 – 430

C–H Photooxygenation of Alkyl Benzenes Catalyzed by Riboflavin Tetraacetate and a Non-Heme Iron Catalyst

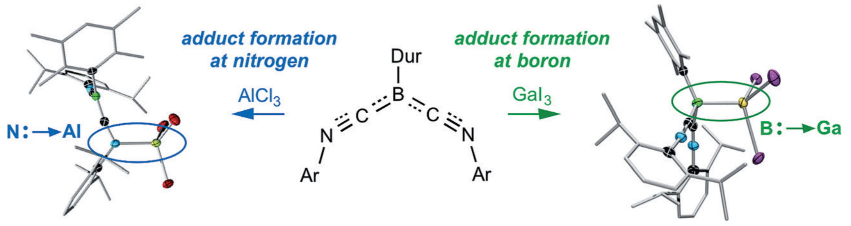


A dual catalyst system consisting of the photocatalyst riboflavin tetraacetate (RFT) and a tris(2-pyridylmethyl)amine iron complex enables efficient visible-light-driven C–H oxygenations of alkyl benzenes. The high catalyst efficiency is attributed to the oxygenation activity of the Fe complex and an increased durability of the photocatalyst owing to iron-catalyzed H_2O_2 decomposition.



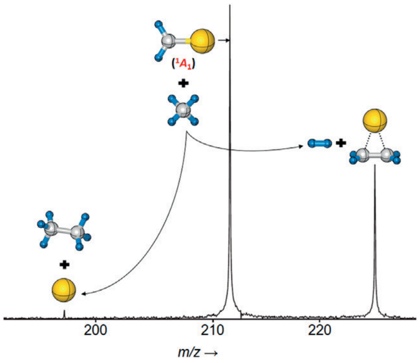
Step by step: $[\text{Cp*As}\{\text{W(CO)}_5\}_2]$ reacts with di-*tert*-butylcarboimidophosphene at low temperatures to give a Lewis acid–base adduct with *tert*-butylisonitrile and an arsaphosphene coordinated by two W(CO)_5 fragments. At room temperature the As–C bond of the arsaphosphene is cleaved homolytically, and two arsaphosphene radicals recombine to form $[\{(t\text{Bu})\text{P}{=}\text{As}{-}\text{As}{=}\text{P}(t\text{Bu})\}\{\text{W(CO)}_5\}_4]$, the first example of a neutral 1,3-butadiene analogue containing heavier Group 15 elements.

Main-Group Chemistry



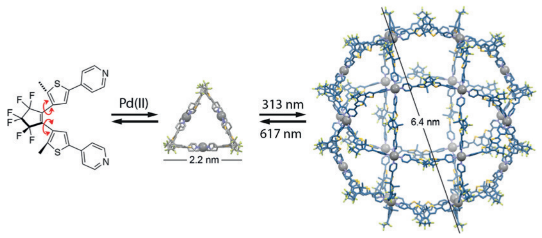
An electron-rich monovalent boron compound is used as a Lewis base to prepare adducts with Group 13 Lewis acids, leading to the first noncluster Lewis adducts between a boron-centered Lewis base and a main-group Lewis acid.

Lewis Adducts



The thermal reactions of the closed-shell, “naked” gold–carbene complex $[\text{Au(CH}_2)]^+$ with methane have been explored by using FTICR mass spectrometry complemented by quantum chemical calculations. The insertion of the carbene ligand into the C–H bond of methane have been addressed mechanistically and the origin of the counterintuitive high reactivity of $[\text{Au(CH}_2)]^+$ towards this most inert hydrocarbon is discussed.

Methane Activation



Lights, action! Irradiation with light of different wavelengths triggers the reversible conversion of small, self-assembled Pd_3L_6 rings based on photochromic dithienylethene ligands into rhombicuboctahedral $\text{Pd}_{24}\text{L}_{48}$ spheres measuring 7 nm across.

Photoswitches

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