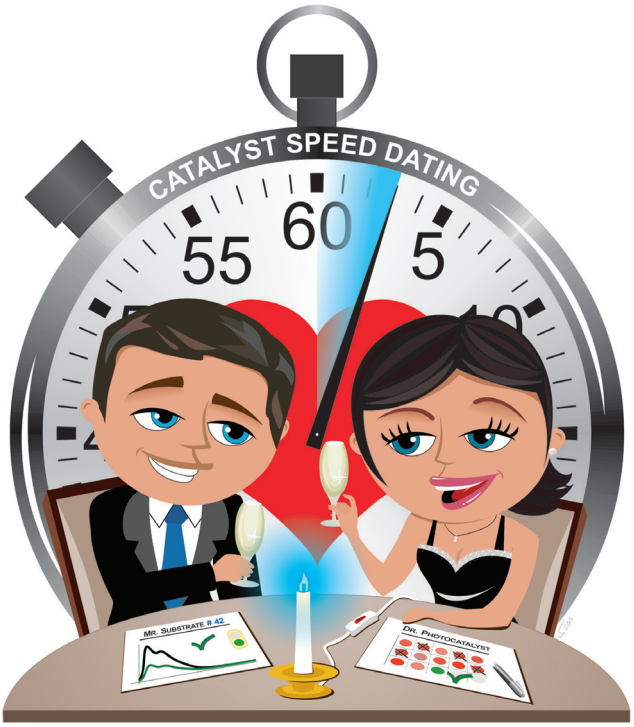
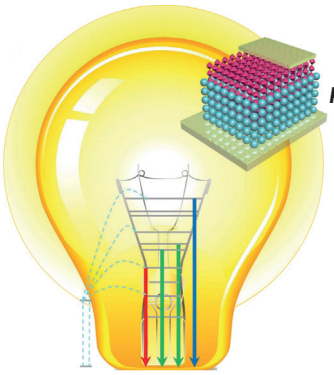
Angewandte International Edition Chemie



... can greatly accelerate the discovery of new chemical reactions. In their Communication on page 4361 ff., F. Glorius et al. describe a conceptually novel mechanism-based screening approach using luminescence spectroscopy to directly investigate the key quenching step in photocatalysis. As illustrated in the cover image, various photocatalysts and potential substrates undergo "speed dating" with the observation of quenching signifying a promising combination that can be applied in new light-promoted reactions.

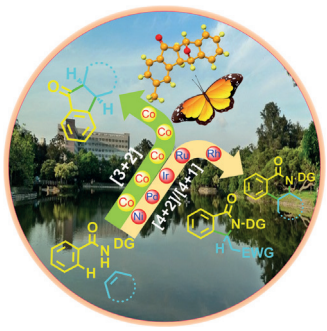
Sustainable Polymers

In their Communication on page 4188 ff., E. Y.-X. Chen et al. report the organocatalytic polymerization of γ-butyrolactone to give a high-molecular-weight metal-free polyester with complete recyclability.



Photovoltaic Devices

In their Communication on page 4280 ff., Z. Lin et al. report a strategy for integrating $NaYF_4$:Yb/Er upconversion nanoparticles as a mesoporous electrode into organolead halide perovskite solar cells.



C–H Activation

In their Communication on page 4308 ff., C.-H. Cheng et al. describe the diastereoselective synthesis of pentacyclic fluorenones from secondary amides and bicyclic alkenes by cobalt-catalyzed C–H activation.

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Service

Author Profile

"My favorite food is noodles. My favorite piece of music is Going Home *(Kenny G) …"* This and more about Zhenfeng Xi can be found on page 4124.

News

J. S. Siegel

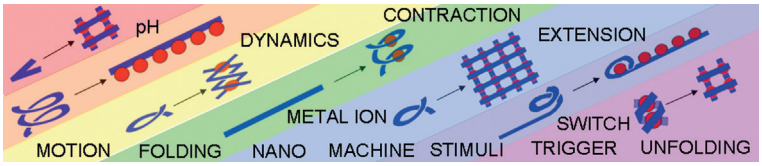
P. J. Stang

M. Antonietti

S. Schlemmer

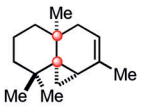
Books

Reviews

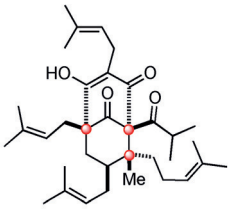


This Review discusses the structural and functional features of polyheterocyclic ligand strands that display designed specific shapes, undergo shape changes on binding of metal cations, and perform various types of pH-responsive motions induced by metal ions.

Raising the bar: The impressive achievements in the total synthesis of complex natural products containing two or three stereogenic contiguous quaternary carbon centers since 1953 are showcased by many creative strategies. The height of the "synthesis bar" can now be raised to consider hitherto unconquered molecules with multiple contiguous quaternary carbon atoms, each residing on a stereogenic carbon atom.

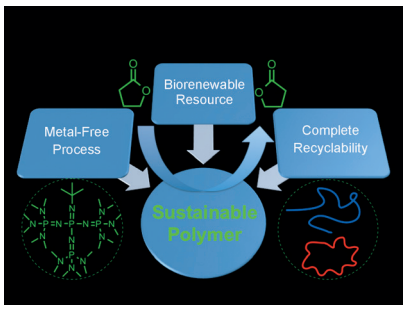


thujopsene
(1953)



hyperforin
(2015)

Communications



Recyclable and renewable: The fast organopolymerization of the biorenewable non-strained γ-butyrolactone has led to a high-molecular-weight metal-free polyester with complete recyclability. The monomer has been long believed to be a non-polymerizable monomer because of its stable five-membered ring structure.

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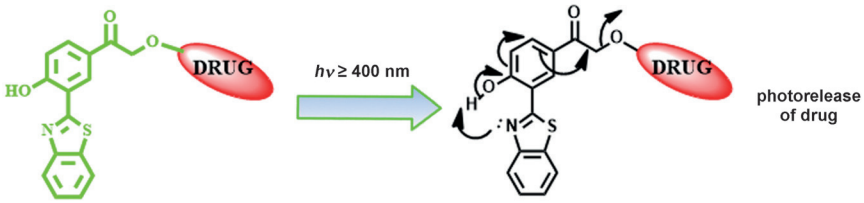
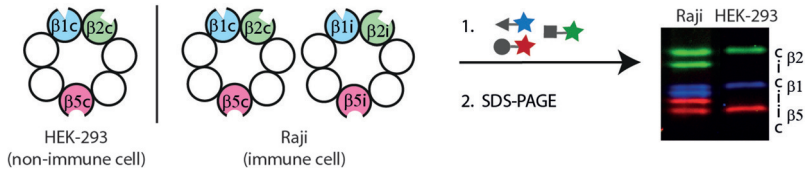


Photoregulated Drug Release

Let it go... The two major limitations for theranostics of the *p*-hydroxyphenacyl (pHP) phototrigger were overcome by incorporating a benzothiazole appendage to enable rapid excited-state intramolecular proton transfer (ESIPT; see picture). The ESIPT effect had two key advantages: It assisted the deprotonation of pHP group for faster release of the anticancer drug chlorambucil and led to a fluorescence color change upon photorelease.

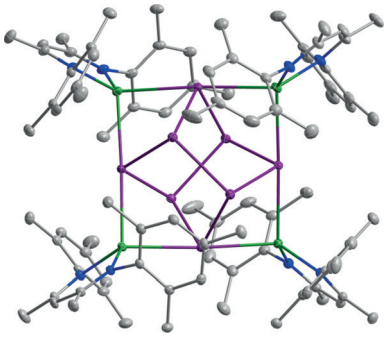
A *p*-Hydroxyphenacyl–Benzothiazole–Chlorambucil Conjugate as a Real-Time-Monitoring Drug-Delivery System Assisted by Excited-State Intramolecular Proton Transfer



Activity-Based Protein Profiling

A cocktail of activity-based probes enables the visualization and relative quantification of the six catalytically active subunits of the constitutive proteasome and the immunoproteasome. Proteasome inhibitors were thus characterized, and specific inhibitors for each subunit were developed. Specific inhibition of the immunoproteasome subunits β5i and β1i proved to be cytotoxic to primary cells from acute lymphocytic leukemia patients.

A Set of Activity-Based Probes to Visualize Human (Immuno)proteasome Activities

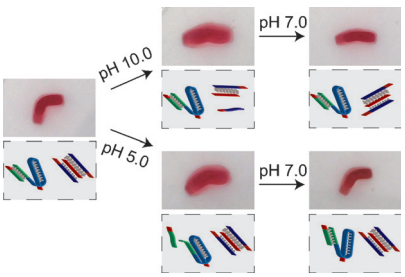


Polystibides

Reduction reactions of distibines Sb_2R_4 (R = Me, Et) with monovalent magnesium complexes $[(L^{1,2}Mg)_2]$ yielded the first tetraanionic polystibides $[(L^{1,2}Mg)_4Sb_8]$ (L^1 = HC[C(Me)N(2,4,6-$Me_3C_6H_2$)]$_2$, L^2 = HC[C(Me)N(2,6-*i*$Pr_2C_6H_3$)]$_2$), in which the central Sb_8 cores adopt realgar-type structures. Atom colors: Mg = green; Sb = purple; N = blue; C = gray.

Synthesis and Structural Characterization of Magnesium-Substituted Polystibides $[(LMg)_4Sb_8]$

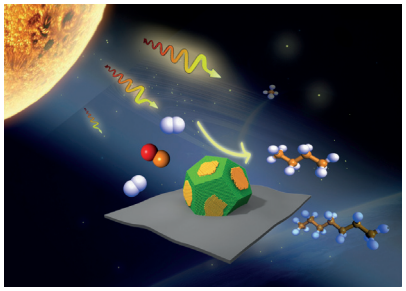
An acrylamide–DNA hydrogel of a defined shape has been synthesized by crosslinking the polymer chains with two different pH-responsive oligonucleotide units. The hydrogel was transformed into a soft, shapeless state by a pH-induced selective dissociation of one of the crosslinker types, while the second crosslinking unit was retained as internal memory.



DNA Nanostructures

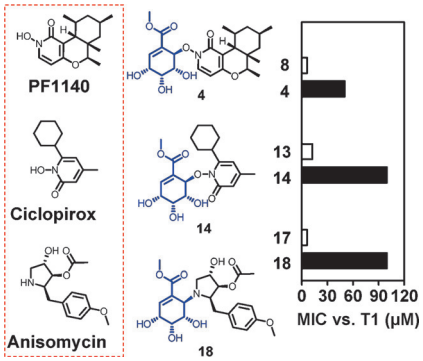
A Shape-Memory DNA-Based Hydrogel Exhibiting Two Internal Memories

Photocatalysis



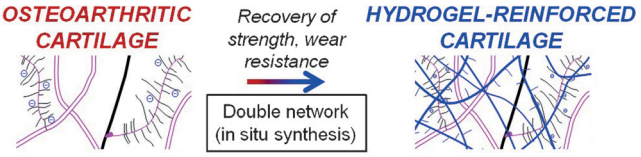
Production of hydrocarbons: Oxide-decorated metal nickel nanoparticle catalysts were prepared and used for the photocatalytic hydrogenation of carbon monoxide to C_{2+} hydrocarbons in visible light. The work highlights the possibility of using solar energy to produce fuels and chemicals under mild reaction conditions.

Natural Products



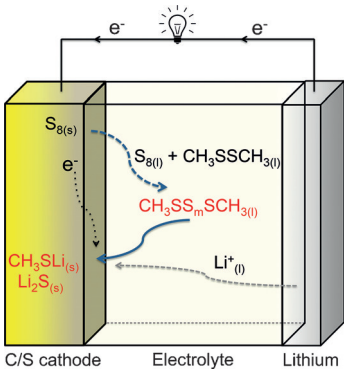
Electrophilic warheads: Fungus-derived shikimate analogues, pericoxide and pericosine A (see picture; blue), have been identified as archetypal chemoreactive natural products that neutralize the antagonistic properties of chemically diverse synthetic and naturally derived antifungal agents and toxins (see picture; left).

Biomaterials

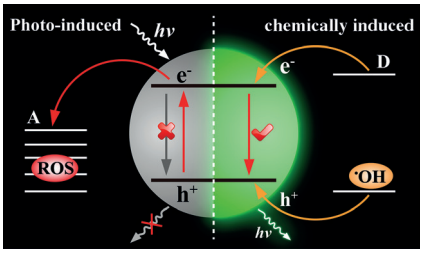


Bring in the reinforcements: Softened and wear-prone articular cartilage is reinforced by a semi-natural–semi-synthetic interpenetrating polymer network. In situ photopolymerization of biomimetic monomers within the tissue increases cartilage strength and wear-resistance. This biomaterials-based approach may hold promise for treating early stage osteoarthritis.

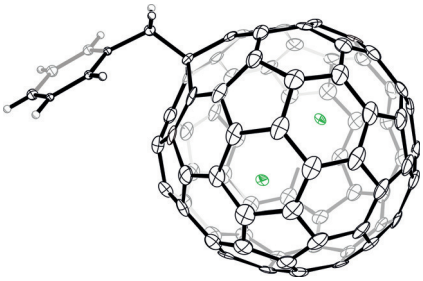
Batteries



Finding the right electrolyte: Dimethyl disulfide (DMDS) was reported as a functional co-solvent for Li-S electrolytes. DMDS enabled an alternative discharge pathway for sulfur cathodes by formation and subsequent reduction of dimethyl polysulfide (DMPS) intermediates, showing a much higher capacity and more stable cycling performance than that of conventional Li–S cells.

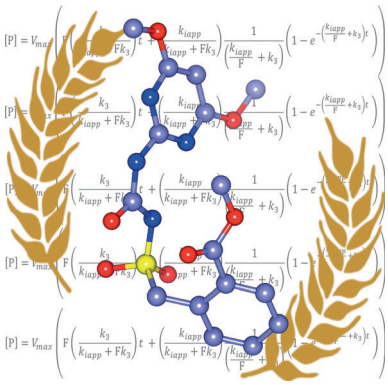


HO• selective: A novel quantum dot (QD) based turn-on luminescent probe for the specific detection of hydroxyl radicals was designed and used for monitoring the endogenous release of such species in living cells. Metal citrate complexes on the surfaces of the QDs play a crucial role as electron donors. Importantly, this luminescent probe does not respond to other reactive oxygen species (ROS).

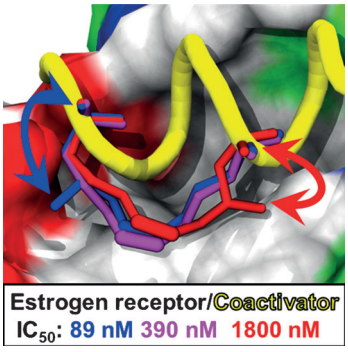


A stable fullerene radical $La_2@I_h$-$C_{80}(C_7H_7)$ was synthesized and fully characterized. The stability of the radical is attributed to the localization of the unpaired electron inside the cage, as suggested by EPR spectroscopy and DFT calculations. Metal–metal bonding is indicated by the La–La distance, which is consistent with the calculated distance, and the localization of the SOMO on the La_2 unit.

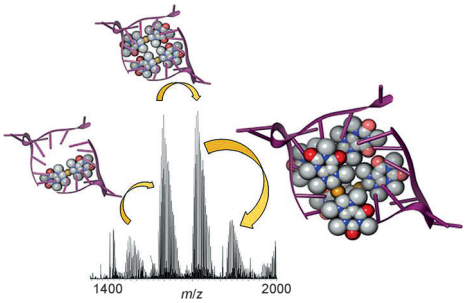
How AHAS-inhibiting herbicides work: Acetohydroxyacid synthase (AHAS) inhibitors, such as bensulfuron methyl (see picture), are successful commercial herbicides; however, their mechanism of inhibition is poorly understood. To address this issue, a new equation is proposed that both accounts for the accumulative and reversible inhibition of AHAS and explains all previous experimental data. Atom colors: C = blue; N = dark blue; O = red; S = yellow.



Branching out: γ-Branched stapling amino acids were synthesized and incorporated into peptides to produce high-affinity inhibitors of the estrogen receptor/steroid receptor coactivator interaction. Some branched stapled peptides were more effective than the unfunctionalized peptide. The influence of 1,5-interactions on peptide conformation was analyzed by circular dichroism, X-ray crystallography, and molecular dynamics.

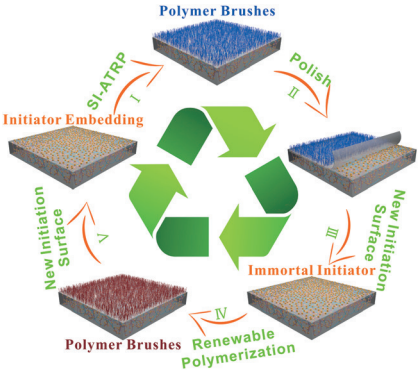


Anticancer Agents



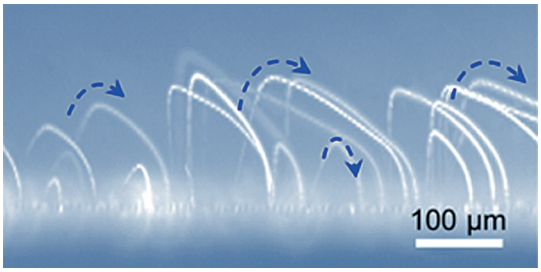
Ready for takeoff: A crystal structure analysis of the adduct formed between $[Au(9\text{-methylcaffein-8-ylidene})_2]^+$ and Tel 23 DNA G-quadruplex is presented. In the adduct, Tel 23 maintains a characteristic propeller conformation, while binding three gold(I) dicarbene moieties at two distinct sites.

Surface Modifications



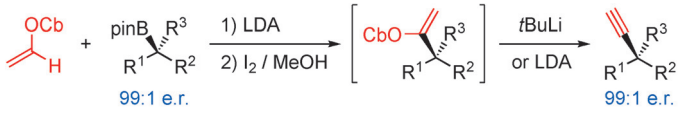
A simple and robust method is reported to repeatedly modify surfaces with polymer brushes through SI-ATRP, based on an initiator-embedded polystyrene sheet. This method outpaces traditional surface grafting technologies owing to unlimited grafting cycles, and it can be combined with carving, micromachining, and hot embossing, and allows stereoselective polymer grafting and metal deposition.

Superhydrophobic Surfaces

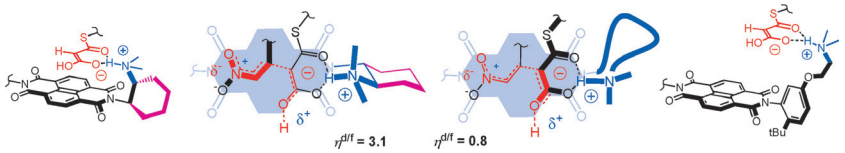


Jumping Jack Flash: Water microdroplets can coalesce and leap over the surface spontaneously along a prescribed direction upon introducing anisotropic micropatterns onto superhydrophobic surfaces. These surfaces offer efficient self-powered and relatively long-distance transport of microdroplets by "relay" coalescence-induced leaping and effective self-sustained microcarriers.

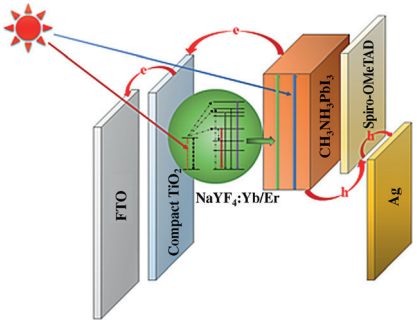
Boronic Ester Reactions



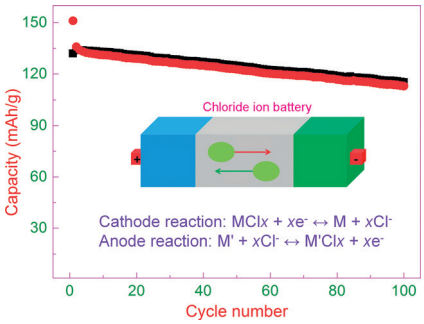
Enantiospecific alkynylation: Enantioenriched secondary and tertiary alkyl pinacolboronic esters undergo enantiospecific deborylative alkynylation through a Zweifel-type alkenylation followed by a 1,2-elimination reaction to give alkynes in high yield and essentially complete enantiospecificity.



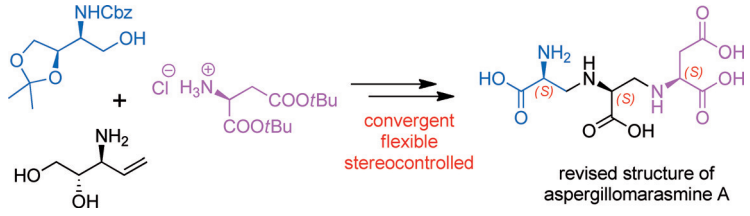
Served on a platter: Simple, compact, and precisely sculpted Leonard turns are introduced to firmly and reliably place reactions on aromatic surfaces, minimizing entropic costs to maximize enthalpic gains. The significant change in selectivity ($\eta^{d/f}$) from less desirable decarboxylation with loose turns (right) to more relevant enolate addition pathways on π-acidic surfaces with rigidified Leonard turns (left) demonstrates the power of this concept.



A strategy for integrating $NaYF_4$:Yb/Er upconversion nanoparticles as a mesoporous electrode into $CH_3NH_3PbI_3$ perovskite solar cells makes it possible to operate the cells with near-infrared light. The in situ integration of upconversion materials as functional components in perovskite solar cells offers flexibility for engineering the device architecture and broadening the use of solar radiation.



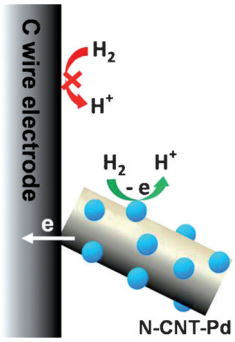
Chloride shuttle: A rechargeable chloride ion battery is based on the reversible transfer of chloride ions between a VOCl cathode and lithium anode. A reversible capacity of 113 mAh g^{-1} can be retained after 100 cycles even at a high current density rating of 2 C. Key: ● Cl^-, ■ MClx (cathode), ■ M′ (anode), → discharging, ← charging.



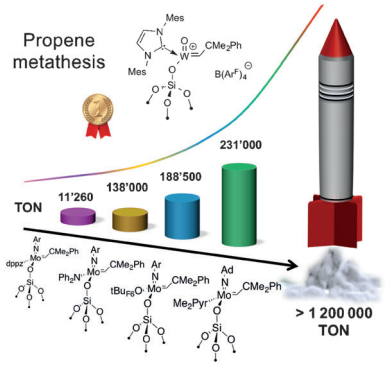
Resistance is futile: The natural product aspergillomarasmine A (AMA) is a potent inhibitor of metallo-β-lactamase-1, which mediates resistance to β-lactam antibiotics. The presented total synthesis of AMA allowed a reassignment of its stereochemical configuration. The synthetic route is amenable to the efficient preparation of analogues for the development of potent and selective metallo-β-lactamase inhibitors.

Electrochemistry

Catalysis at the nanoscale: The cyclic voltammetric responses of individual palladium-coated nitrogen-doped multi-walled carbon nanotubes (N-CNT-Pd; see picture) were studied. The nanoparticles acted as individual nanoelectrodes that catalyzed the hydrogen-oxidation reaction.

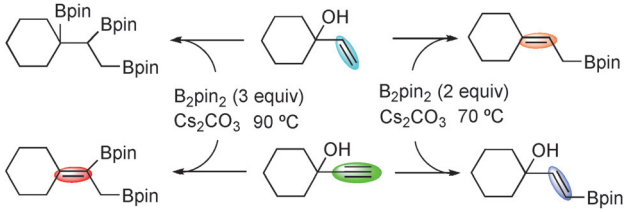


Supported Catalysts



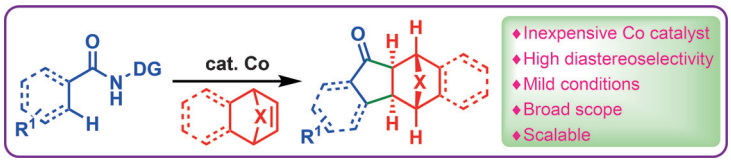
Like a rocket: A well-defined silica-supported cationic N-heterocyclic carbene tungsten oxo alkylidene catalyst ($B(Ar^F)_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4$, Mes = mesityl) was synthesized and fully characterized by elemental analysis, infrared spectroscopy, and solid-state NMR spectroscopy. The catalyst demonstrated very high activity for the metathesis of olefins.

Borylation

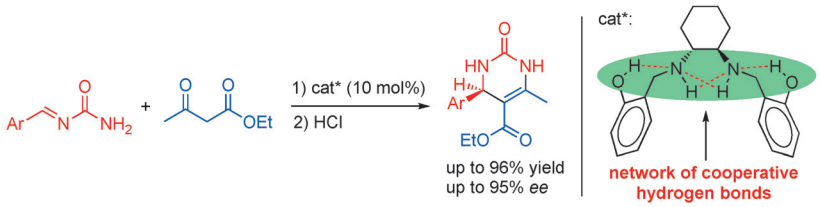


A transition-metal-free allylic borylation of tertiary allylic alcohols provides access to new allylic boronates. The reactions were carried out in the presence of 15 mol% of Cs_2CO_3 and MeOH to promote the Lewis acid–base adduct formation $[Hbase]^+[MeO\text{-}B_2pin_2]^-$, which may be responsible for generating unprecedented 1,2,3-polyborated products.

C–H Activation

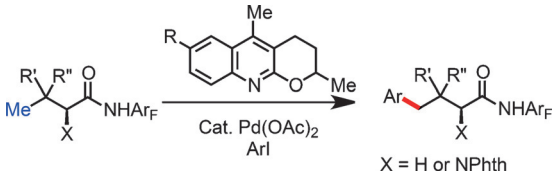


[3+2] instead of [4+2] or [4+1]: The diastereoselective [3+2] annulation of secondary amides with alkenes proceeds by cobalt-catalyzed C–H activation and intramolecular nucleophilic addition to the amide functional group under mild conditions. Mechanistic studies suggest that the C–H bond cleavage is the rate-limiting step.



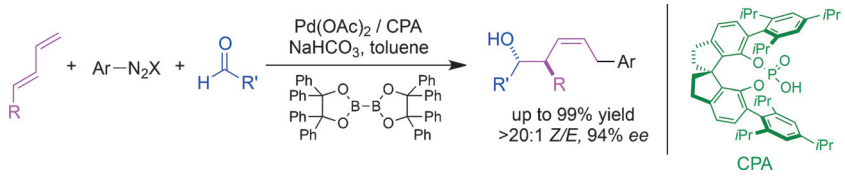
Caught in the net: The standard roles that the actors (nucleophile, electrophile, and catalyst) perform during the catalytic act in the arena of bifunctional catalysis were switched in the search for bioinspired organocatalysts. It was thus found that the network of hydrogen bonds provided by salan derivatives catalyzed the Mannich reaction of arylideneureas with acetoacetates in an enantioselective, biomimetic manner (see scheme).

Asymmetric Catalysis



Pd^{II}-catalyzed arylation of γ-C(sp^3)–H bonds of aliphatic acid-derived amides was developed by using quinoline-based ligands. Various γ-aryl-α-amino acids were prepared from natural amino acids using this method. The influence of ligand structure on reactivity was also systematically investigated.

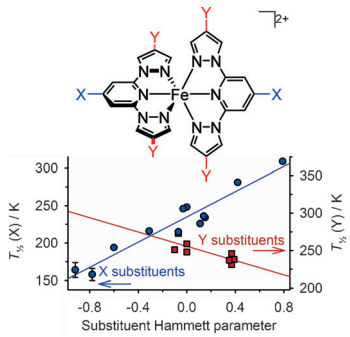
C–H Activation



Catalysis combo: A highly selective multicomponent carbonyl allylation reaction of 1,3-butadienes, aryldiazonium tetrafluoroborates, and aldehydes has been established under combined palladium acetate and chiral anion phase-transfer catalysis. The protocol leads to the assembly of chiral *Z*-configured homoallylic alcohols in high yields and with excellent levels of enantioselectivity.

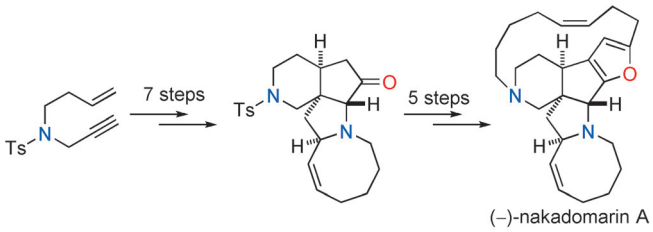
Asymmetric Catalysis

Highs and lows: The low-spin state of the complex shown is stabilized by electron-withdrawing pyridyl "X" substituents, but also by electron-donating pyrazolyl "Y" substituents. DFT calculations reproduce these results, which arise from competing influences of pyridyl and pyrazolyl ligand substituents on Fe–L σ and π bonding.



Spin State

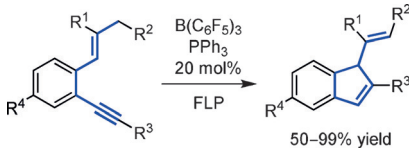
Marine Alkaloids



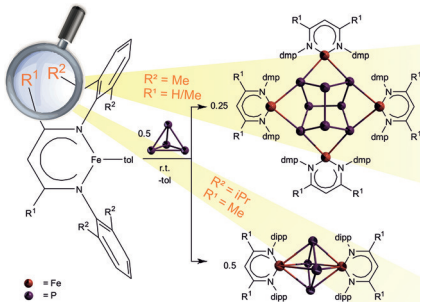
The later the better: A highly efficient 12-step synthesis of (−)-nakadomarin A is reported. The key tetracyclic ketone intermediate was constructed from a simple enyne in seven steps. As the furan is introduced at a later synthetic stage, this intermediate may have potential in the syntheses of related marine alkaloids such as manzamine A and ircinal A.

FLP Catalysis

Cycloisomerization without a metal: The first FLP-catalyzed C–C bond forming reaction is described as proceeding through a cycloisomerization/protodeborylation sequence. The reaction mechanism is supported by X-ray crystal structure analysis of intermediates, kinetic experiments, and by quantum-mechanical calculations.

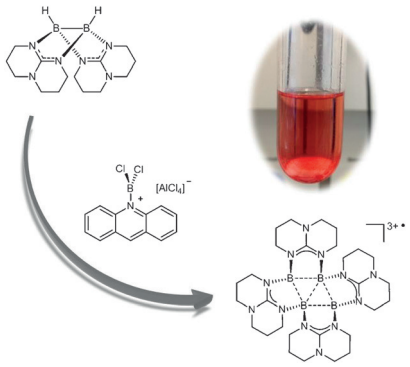


P_4 Activation

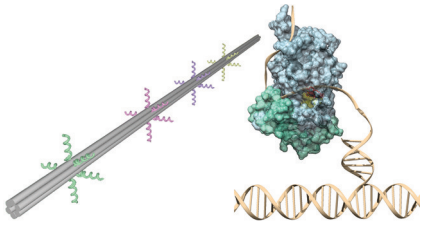


Depending on the size of the substituents of the *N*,*N*′-diarylated β-diketiminato ligands, iron(I) complexes activate white phosphorus in different ways. Small substituents result in dimerization with formation of a realgar-like P_8 ligand at the center of a tetranuclear complex; larger substituents lead to planarization in dinuclear *cyclo*-P_4 complexes.

Boron Compounds

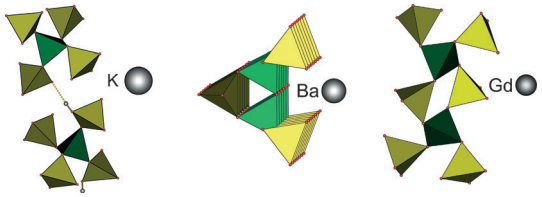


Share and share alike: Reaction of the doubly base-stabilized diborane(4) [HB(hpp)]$_2$ with the strong hydride abstraction reagent [(acridine)BCl_2][$AlCl_4$] leads to the unprecedented red-colored tetraborane(4) $[B_4(hpp)_4]^{3+\bullet}$ with a rhomboid B_4 skeleton and four-center, five-electron bonding.



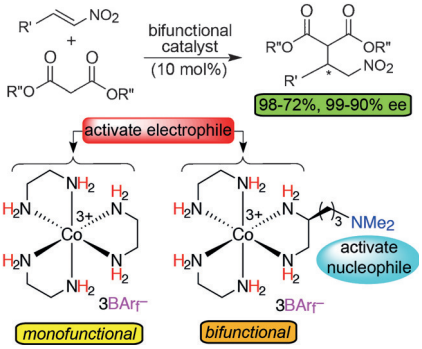
In nature, relaxase proteins are involved in the conjugative transfer of plasmids between bacteria. Here it is shown that their specificity for a single-stranded DNA target, their good orthogonality, and their binding properties can also be utilized for the functionalization of DNA nanostructures with proteins.

DNA Nanotechnology



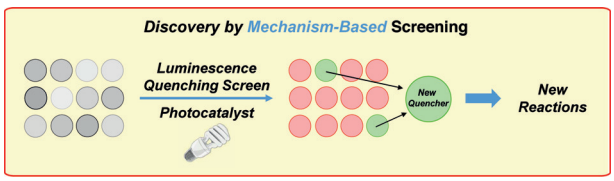
Extension of structural variability is the feature of the first borosulfates of a divalent and a trivalent cation showing band-silicate (see picture; middle: borate tetrahedra green, sulfate tetrahedra yellow) and cyclosilicate topologies (right), which were obtained by a new synthetic approach. Moreover, the first hydrogen-borosulfate is presented (left; small spheres: H).

Borosulfates



Two are better than one: Unlike the catalyst Λ-$[Co(en)_3]^{3+}$ 3 BAr_f^-, the bifunctional tertiary-amine-containing analogue Λ-**3c**$^{3+}$ 3 BAr_f^- effects highly enantioselective additions of alkyl malonates to β-aryl- and β-alkylnitroethenes. The efficacy diminishes as the $(CH_2)_3$ tether is shortened or lengthened.

Bifunctional Catalysts



Enlightened! A mechanism-based screening approach can accelerate discovery in photocatalysis. It focuses on a single mechanistic step of a reaction class: the quenching step central to photocatalytic transformations. Luminescence spectroscopy was used to screen 100 compounds, identifying two promising substrate classes. A second, more-focused screen provided mechanistic insights for developing proof-of-concept reactions.

Screening Methods

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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