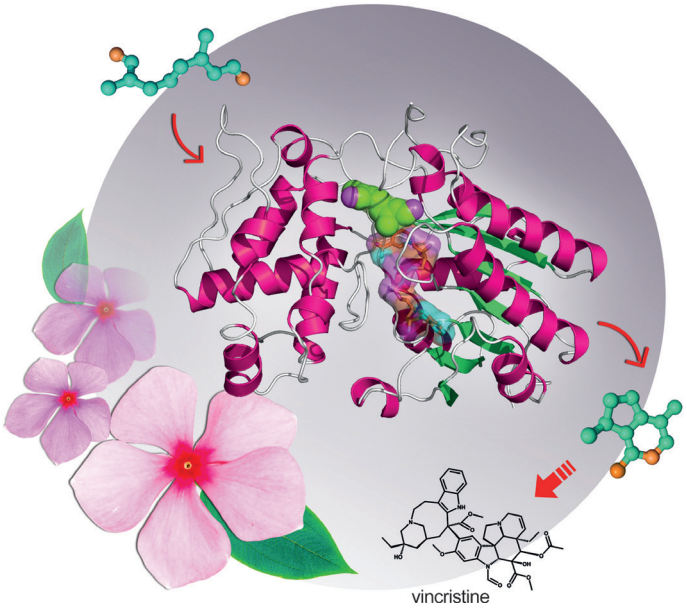
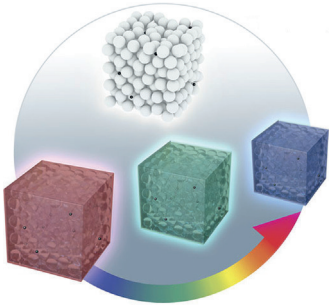
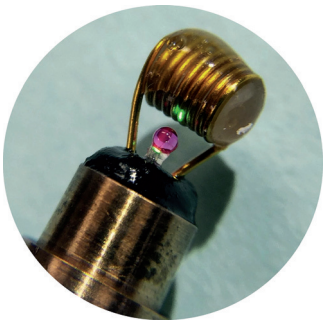


... iridoid synthase (IRIS) produces nepetalactol, a precursor for drugs such as vincristine. In their Communication on page 15478 ff., E. Oldfield, R.-T. Guo, and co-workers present the structures of IRIS from Cantharanthus roseus in complex with NADP and the substrate 10-oxogeranial. The structures show how nepetalactol and the byproduct oxo-citronellal are formed and provide insight into the biosynthesis of iridoids and cardiac glycosides.



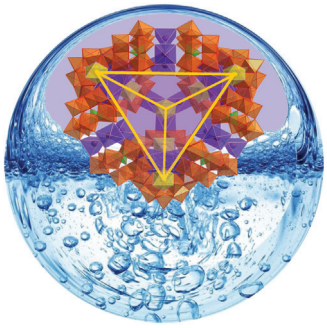
Angle-Independent Structural Color

In their Communication on page 15368 ff., Y. Takeoka et al. report on thermally tunable hydrogels displaying angle-independent structural colors that were prepared from colloidal amorphous array templates and carbon black.



NMR Spectroscopy

W. H. Casey et al. report in their Communication on page 15444 ff. how a ruby sphere coupled to a fiber-optic cable allows pressure estimates in a new NMR probe design.



Polyoxometalates

M. Ibrahim, A. K. Powell et al. present on page 15574 ff. the POM system with the largest number of 4f ions reported to date. It contains 30 Dy^{III}, 8 Co^{II}, and 108 W^{VI} metal centers and exhibits single-molecule magnet behavior.

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Service

Author Profile

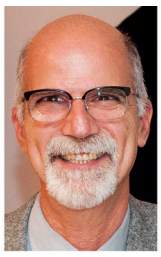
„In the future I see myself causing university administrators to weep in frustration. The biggest challenge facing scientists is our smothering and reflexive elitism …“
This and more about William H. Casey can be found on page 15326.

News


S. Cosnier


D. Lincot


W. B. Motherwell

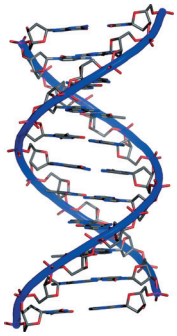

M. Prato


K. Grela

Books

Highlights

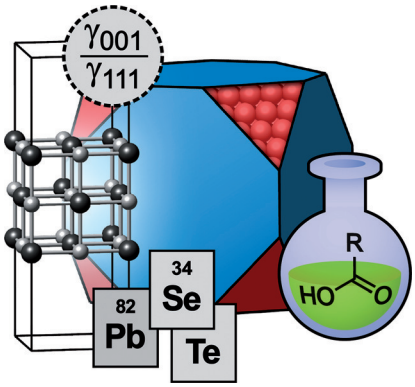
DNA Repair



DNA is constantly damaged by various endogenous and exogenous events. Repair systems constantly scan the genome for DNA lesions and replace damaged and mismatched bases, which finally enables the complex DNA double strand to store genetic information. This year's Nobel Prize in Chemistry was awarded to pioneers in this field, T. Lindahl, P. Modrich, and A. Sancar.

Minireviews

Nanostructures

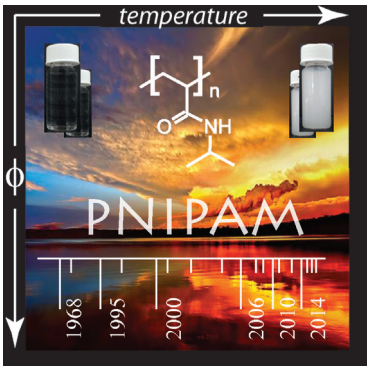


Nanocrystals, made to measure? Skillful links between theory and experiments promise new insight into the chemistry of nanoscale materials. This Minireview describes how such bridges can be built for group IV chalcogenides, from free surfaces to nanocrystals, and with the long-term goal of enabling rational synthesis planning.

Reviews

Polymer Phase Diagrams

During the past 50 years, PNIPAM became the leading member of the growing families of thermoresponsive polymers and of stimuli-responsive polymers in general. Its thermal response is unanimously attributed to its phase behavior. Yet, in spite of 50 years of research, a coherent quantitative picture remains elusive. This Review aims to alert to open questions in this field.



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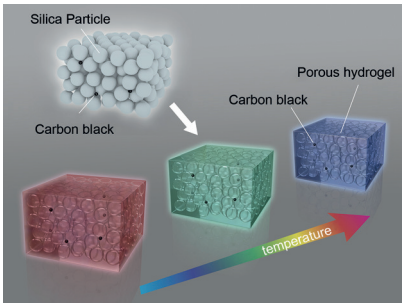
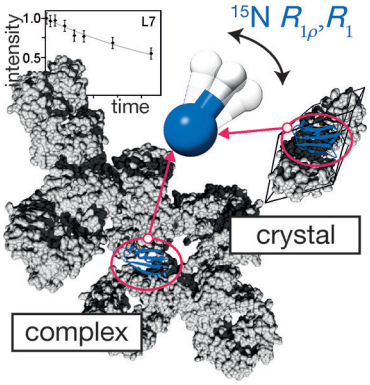
Communications

Colored hydrogels: Thermally tunable hydrogels displaying angle-independent structural colors were prepared using colloidal amorphous array templates and a small amount of carbon black (see picture). The brightly colored hydrogels rapidly and reversibly changed hues that varied widely depending on the water temperature.

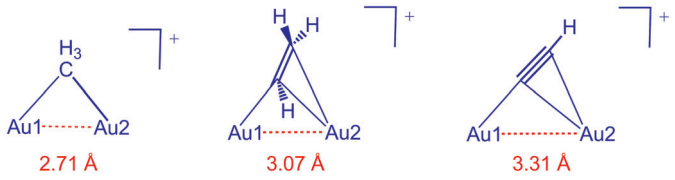


Soft Matter



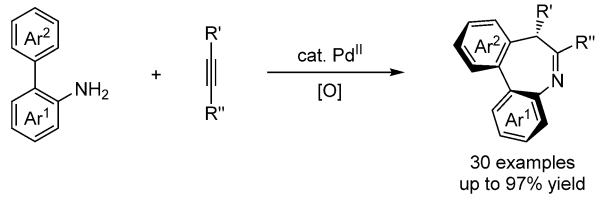
Protein dynamics: To investigate the influence of different intermolecular interactions on the protein dynamics extensive widespread site-specific ^{15}N relaxation measurements were compared for a protein GB1 in a crystal and in an antibody complex with a molecular weight of more than 300 kDa (see picture). The proposed approach allows to directly access dynamics of a protein in large protein complexes.

Solid-State NMR Spectroscopy



The first methyl-bridged cationic digold complex, [(^{Dipp_2}ArMe$_2$P)Au(μ-CH$_3$)Au(PMe$_2$Ar^{Dipp_2})]$^+$ (Ar^{Dipp_2} = C$_6$H$_3$-2,6-(C$_6$H$_3$-2,6-*i*Pr$_2$)$_2$), is stabilized by a bulky terphenylphosphine ligand. The aurophilic interaction in this complex is comparable to that in {Au$_2$(μ-H)}$^+$ species and stronger than in the vinyl- and acetylide-bridged analogues (see scheme).

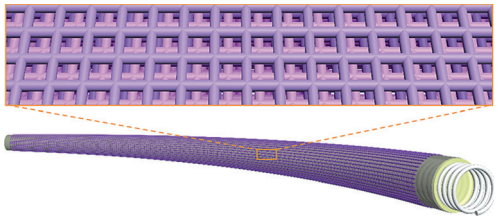
Digold Complexes



Link up: The title reaction has been developed for building a seven-membered N-heterocyclic architecture containing a biaryl linkage. This method is applicable to a wide range of unprotected *o*-arylanilines and internal alkynes, and results in the chemoselective preparation of imine-containing dibenzo[*b*,*d*]azepines in high yields with excellent diastereoselectivity with regard to the two types of stereogenic elements.

C–H Activation

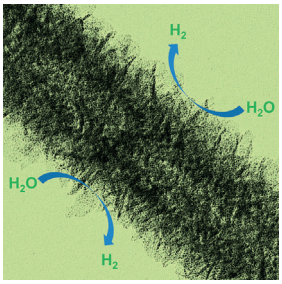
Metal–Air Batteries



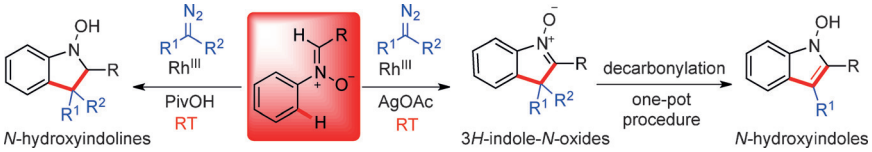
Fiber-shaped zinc–air batteries were realized with excellent electrochemical properties by designing aligned and cross-stacked carbon nanotube sheets (see picture). The batteries were flexible and stretchable, which is particularly promising for powering portable and wearable electronic devices.

Hydrogen Evolution

From the same sheet: Hierarchical β-Mo_2C nanotubes constructed of ultrathin nanosheets are designed and synthesized. Benefitting from ultra-small primary nanocrystallites, a large exposed surface, fast charge transfer, and unique tubular structure, the as-prepared hierarchical β-Mo_2C nanotubes exhibit excellent electrocatalytic performance for the hydrogen evolution reaction.



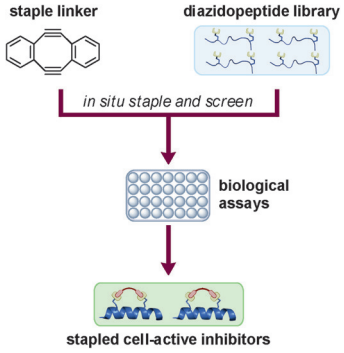
Heterocycle Synthesis



A flurry diazo of activity: Reported herein is the first rhodium(III)-catalyzed [4+1] C–H oxidative cyclization of nitrones with diazo compounds to access 3*H*-indole-*N*-oxides. More significantly, this reaction proceeds at room temperature and has been extended to the synthesis of *N*-hydroxyindoles and *N*-hydroxyindolines. Piv = pivaloyl.

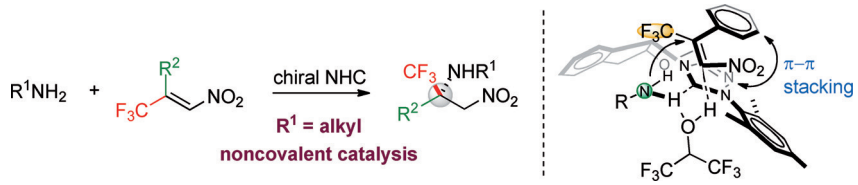
Biomolecular Recognition

Catch a match: The best biomolecular partner for a given calixarene host can be found by fishing in a crude HeLa cellular extract. In particular, a simply designed *p*-acetamidocalix[4]arene was able to specifically fish out protein disulfide isomerase (PDI). Independent studies confirmed its considerable affinity for PDI (K_D = 11 μM), the inhibition of PDI chaperone activity, and cytotoxic activity against two cancer cell lines.



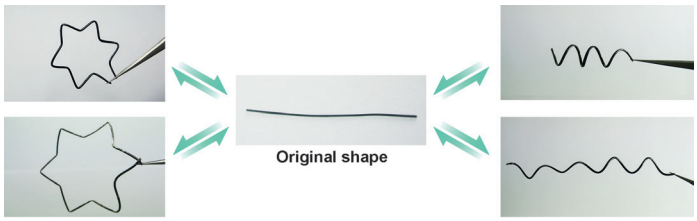
More strain, more gain: A strained cyclodialkyne was used to staple diazidopeptides directly in the medium of a cell culture assay. This in situ approach is simple to conduct and enables combined stapling and screening for cell-active stapled peptides in a parallel, high-throughput format. The method was applied to the p53/MDM2 interaction as proof of principle, and a new inhibitor was identified and its crystal structure with MDM2 obtained.

Peptide Stapling



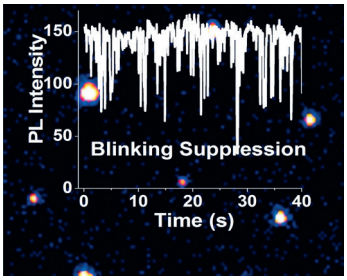
No longer left out in the cold: A chiral N-heterocyclic carbene (NHC) promoted the title highly enantioselective aza-Michael reaction of aliphatic amines, which were incompatible with previously developed catalytic systems owing to their basicity. HOMO-raising activation of the amine nucleophile enabled the preparation of chiral trifluoromethylated 1,2-diamines in high yield (up to 99%) with up to 98% *ee* (see scheme).

Asymmetric Conjugate Addition



A smart supercapacitor: A shape-memory supercapacitor was developed by winding carbon nanotube sheets on a shape-memory polyurethane substrate (see picture). Its electrochemical performances are well maintained during deformation, at the deformed state and after the recovery.

Energy Storage

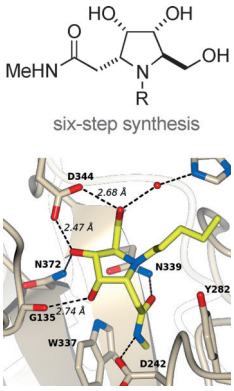


Don't blink: The luminescence of $CsPbBr_3$ perovskite nanocrystals (NCs) is more suitable for high-definition display applications than the traditional CdSe-based colloidal quantum dots. Colloidal dispersions, single-NCs, and thin films of $CsPbBr_3$ NCs all exhibit nearly ideal photoluminescence (PL) quantum yield (QY), narrow spectral width, negligible influence of FRET and self-absorption, temperature-independent chromaticity, and suppression of blinking off time.

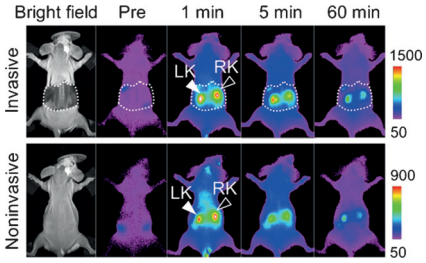
Photoluminescence

Enzyme Inhibitors

On the brain: An epimerization strategy provides direct access to a range of stereoisomeric iminocyclitol inhibitors of O-GlcNAcase (OGA), the enzyme responsible for catalyzing removal of O-GlcNAc from nucleocytoplasmic proteins. Binding of these inhibitors to a bacterial homologue of OGA was obtained, and it was shown that they permeate in rodent brains.

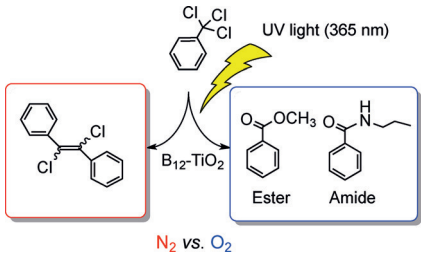


In Vivo Imaging



Kidney imaging with gold nanoparticles: Enabled by renal clearable NIR-emitting gold nanoparticles, kidney clearance kinetics can now be noninvasively monitored at high contrast with in vivo fluorescence techniques.

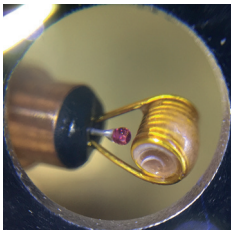
Hybrid Catalysts

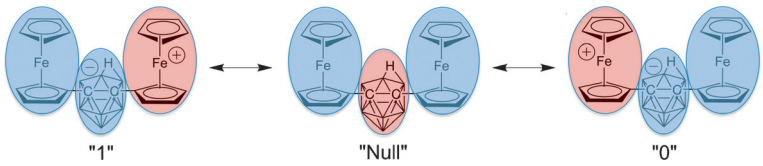


An oxygen switch in catalysis with a cobalamin derivative (B_{12})-TiO_2 hybrid catalyst for the dechlorination of trichlorinated organic compounds has been developed. Immobilized B_{12} transformed trichlorinated organic compounds into esters and amides by UV light irradiation under mild conditions (in air at room temperature), while dichlorostilbene was formed in a nitrogen atmosphere from benzotrichloride.

Geochemistry

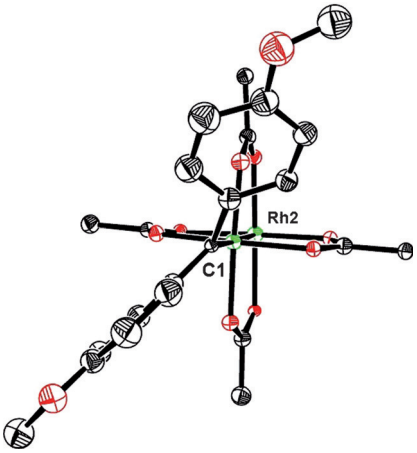
A ruby sphere coupled to a fiber-optic cable allows pressure estimates in a new NMR probe design (see picture). Experiments can be conducted in aqueous solutions at pressures corresponding to those at the base of the Earth's continental crust.





Zwitterionic molecular switches: A neutral mixed-valence compound has been synthesized and characterized. Spectroscopic data, in conjunction with TD-DFT calculations, indicate a bridge-mediated charge transfer that allows for an all-neutral null state vital to QCA molecular switch applications.

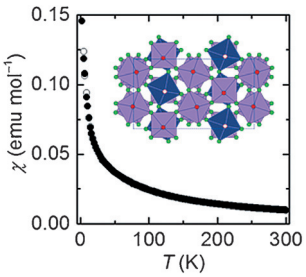
Molecular Switches



Let's have a look: Despite their eminent importance in catalysis, there was until now no X-ray structure of a dirhodium tetracarboxylate carbene complex that features the prototypical reactivity of these carbenes. This gap is now closed (see picture). Moreover, such species were found amenable to transmetalation with Au^{I}, thus opening a practical new route to systematic investigations into gold carbenes.

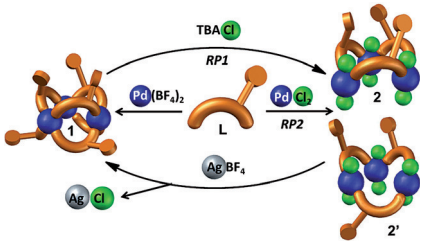
Carbene Complexes

All in a spin: Antiferromagnetic crystalline solids with a kagome network of $S = {}^{1}/_{2}$ ions are desired as realizations of two-dimensional quantum spin liquids. Until recently, the few examples of these materials were all based on Cu^{2+} ions. Now, the ionothermal synthesis, structure, and magnetic properties of a family of inorganic–organic hybrid solids that contain antiferromagnetic kagome layers of $S = {}^{1}/_{2}$ V^{4+} ions is presented.



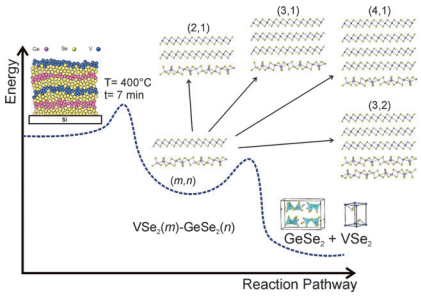
Antiferromagnetic Solids

Chiral water lily: Chiral non-symmetrical bispyridyl ligands coordinate with tetravalent Pd^{II} into large symmetrical enantiomerically pure complex Pd_3L_6 with 60 chiral centers in its structure. Chloride can convert this molecule into smaller $Pd_3L_3Cl_6$, and this process can be easily reversed by addition of silver cations.



Chiral Complexes

Layered Structures

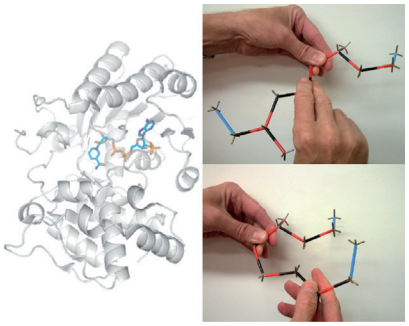


Layered cake: The modulated elemental-reactant technique provides a unique route to the targeted synthesis of new van der Waals heterostructures. VSe_2 and $GeSe_2$ were selected as 2D building blocks to inhibit cation intermixing. The kinetic control offered by this approach enabled heterostructures with varying stacking sequences to be prepared.

Monolayers

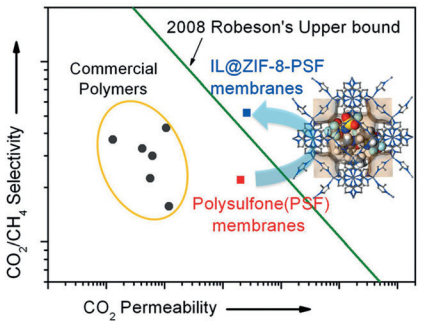
Atomically thin two-dimensional γ-boron films were synthesized on copper foils by a scalable chemical vapor deposition method. The experimentally obtained optical band gap of around 2.25 eV is close to that determined by first-principles calculations (2.07 eV). The strong photoluminescence of the material suggests that the monolayer is a direct band gap semiconductor.

Biosynthesis



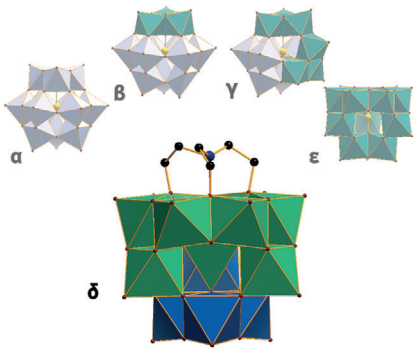
You spin me round: X-ray structures of iridoid synthase show binding of a *transoid* substrate, which serves as a model for the catalytic mechanism of progesterone reductase. Formation of the iridoid product requires rotation about C1–C2 to form the *cisoid* isomer, and rotation about C4–C5 to enable cyclization and lactol production.

Zeolite Nanocages

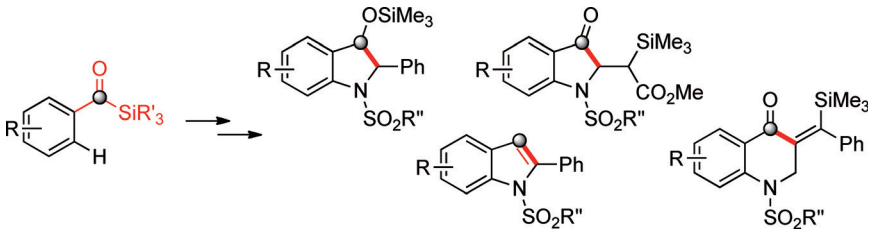


Filling the cavity: A room temperature ionic liquid (IL) was incorporated into ZIF-8 nanocages by ionothermal synthesis, reducing the effective cage size of ZIF-8 and enabling molecular sieving of CO_2 over bulky N_2 and CH_4.

Trapping an elusive δ-Keggin isomer: A simple one-pot reaction led to the isolation and characterization of the first polyanionic δ-Keggin isomer, $[H_2W_4V_8(VO_4)O_{33}(C_6H_{13}NO_3)]^{5-}$. The cluster showed interesting cation-modulated photochromism, and the coordination of the $C_6H_{13}NO_3$ ligands as tripods contributes to the stabilization and photochromic properties of the elusive isomer.

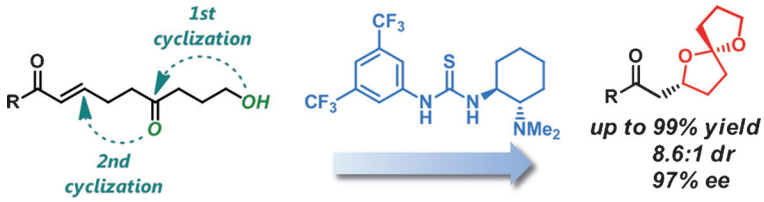


Polyoxometalates



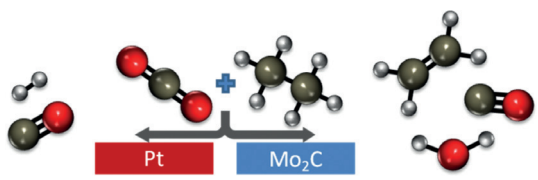
Getting around: The *ortho*-amidation of aroylsilanes with sulfonyl azides in the presence of an iridium catalyst occurs in a highly efficient manner with broad tolerance to substituents on all the reaction partners. After N-functionalization, the products can undergo photochemically or thermally induced cyclization reactions to give N-heterocyclic compounds in high yields.

C–H Functionalization



Around and around: A catalytic asymmetric synthesis of spiroketals through an intramolecular hemiacetalization/oxy-Michael addition cascade with a bifunctional aminothiourea catalyst was developed. This method offers facile access to spiroketal frameworks bearing an alkyl group at the 2-position. Optically active (2*S*,5*S*)-chalcogran, a pheromone from the six-spined spruce bark beetle, and a derivative were readily synthesized from the bicyclic reaction product.

Asymmetric Synthesis

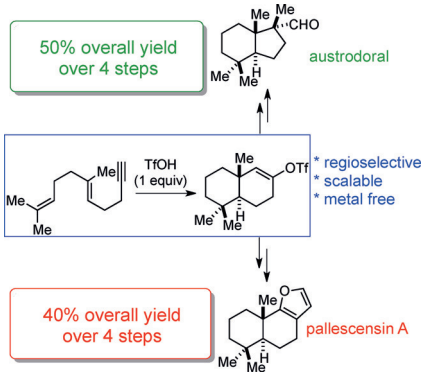


Dry reforming of ethane using CO_2 as oxidant over Pt- and Mo_2C-based catalysts is reported. The two pathways of the reaction (see picture) were controlled by the choice of catalyst.

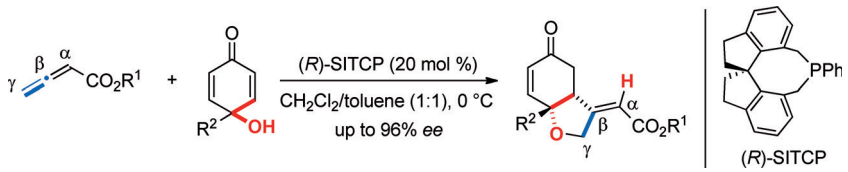
Heterogeneous Catalysis

Cyclization Reactions

Cyclic alkenyl triflates are easily available through a new reaction based on a cationic cyclization process. Extension of the method to biomimetic polycyclization reactions allows the selective synthesis of interesting polycyclic core skeletons, including the terpenes austrodoral and pallescensin A.

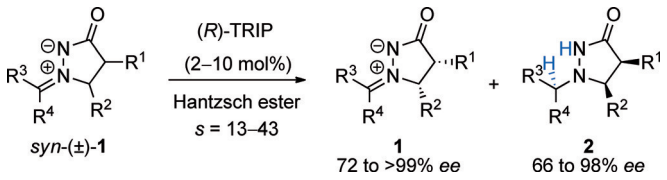


Annulations



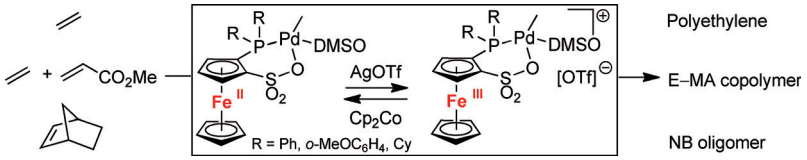
Domino effect: An enantio-, diastereo-, regio-, and chemoselective phosphine-catalyzed β,γ-umpolung domino reaction of allenic esters with dienones has been developed for the first time. The designed sequence involving oxy-Michael and Rauhut–Currier reactions produced highly functionalized tetrahydrobenzofuranones bearing a chiral tetrasubstituted stereogenic center in up to 96% *ee*.

Asymmetric Catalysis

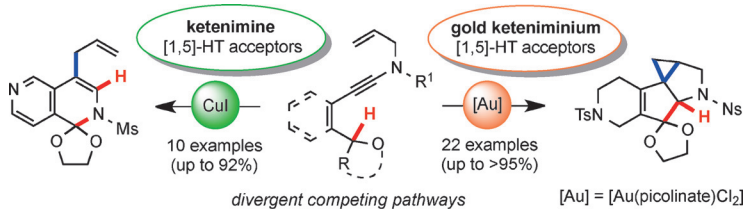


Resolution by reduction: In the first enantioselective reduction of azomethine imines, the Brønsted acid (*R*)-TRIP catalyzes the kinetic resolution ($s = 13$–43) of complex azomethine imines derived from intermolecular alkene aminocarbonylation. Both the pyrazolidinone products (**2**) and recovered azomethine imines (**1**) are enantioenriched sources of complex hydrazines and β-amino carbonyl compounds.

Olefin Polymerization

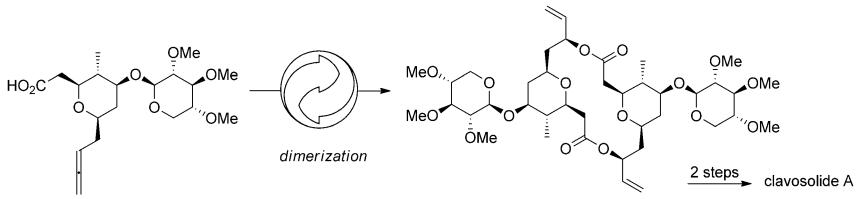


From one to another: Interconversion between the neutral and oxidized forms of a series of Pd complexes with ferrocene-bridged phosphine sulfonate ligands was demonstrated. The neutral and oxidized Pd catalysts had dramatically different activities in ethylene polymerization, ethylene/methyl acrylate (E–MA) copolymerization, and norbornene (NB) oligomerization.



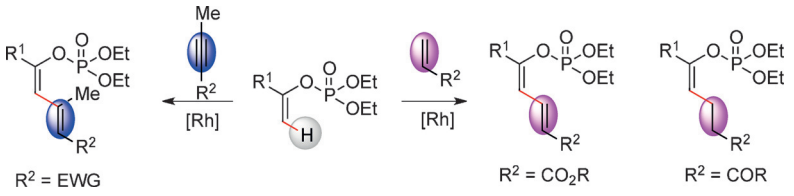
CH CH CHanges: Divergent cycloisomerization reactions of *N*-allyl ynamides with simple catalysts provided access to complex and densely functionalized polycycles. Structure–reactivity studies revealed competing processes involving C–H insertion upon activation of the ynamides as gold–keteniminium or ketenimine intermediates (see scheme; HT = hydrogen transfer).

Cyclization Reactions



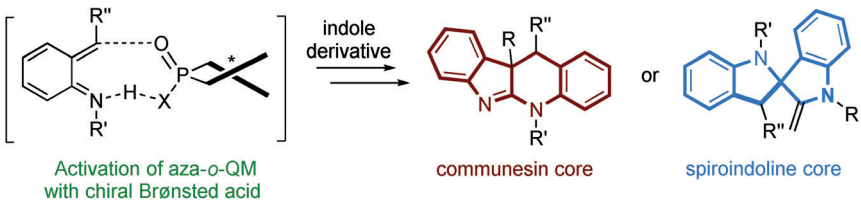
Better late than early: The natural product clavosolide A features a C_2-symmetric core. A rhodium-catalyzed dimerization reaction involving the regio- and diastereoselective addition of carboxylic acids to allenes (see scheme) provided rapid access to this complex structure in only eight steps from penta-3,4-dienal and a readily accessible chiral crotyl-transfer reagent. The method is broadly applicable and suited to late-stage diversification.

Natural Products Synthesis



P points the way: A direct C–H functionalization of enol phosphates was developed. The method is applicable to a variety of coupling partners, including activated alkenes, alkynes, and allenes, and it leads to the formation of alkenylated and hydroalkenylated enol phosphates through the action of the phosphate directing group. The utility of the coupling products are demonstrated by further transformations into synthetically useful building blocks.

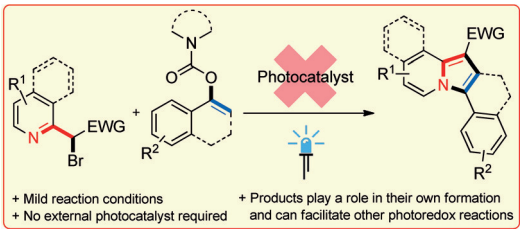
Cross-Coupling



Two protocols have been developed for the regiodivergent, asymmetric Brønsted acid catalyzed addition of indoles to in situ generated aza-*ortho*-quinone methides. Furthermore, a new addition spirocyclization sequence leads, depending on the indole derivative, to communesin and spiroindoline cores with quaternary stereocenters.

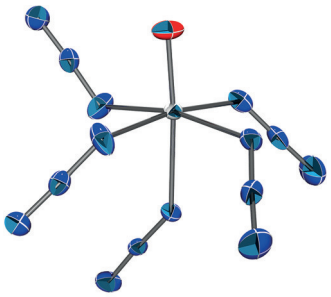
Asymmetric Synthesis

Photomediated Synthesis



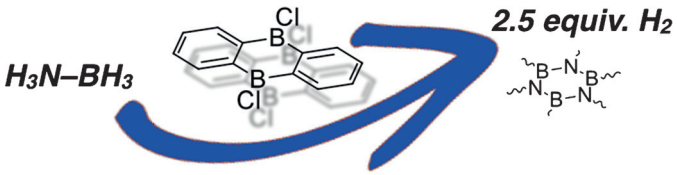
Take it away! A visible-light-mediated synthetic route towards valuable polycyclic indolizine structures has been developed. This method, which proceeds under mild conditions, does not require an external photocatalyst (see scheme, EWG = electron-withdrawing group). Mechanistic studies indicate that the indolizine products themselves may be in some way involved in mediating and accelerating their own formation.

Azide Complexes

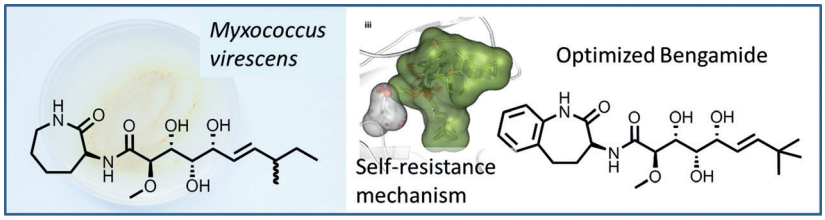


Mo and W make an impact: A series of novel molybdenum(V) and tungsten(VI) oxoazides were obtained and characterized. $[MoO(N_3)_3]$ and $[WO(N_3)_4]$ were obtained by fluoride–azide exchange from $[MOF_4]$ and Me_3SiN_3 as very friction- and impact-sensitive solids. With CH_3CN, $[MoO(N_3)_3]$ and $[WO(N_3)_4]$ form stable acetonitrile adducts. The reactions of $[MoO(N_3)_3]$ with 2,2′-bipyridine and N_3^- afforded $[(bipy)MoO(N_3)_3]$ and $[MoO(N_3)_5]^{2-}$, respectively.

Hydrogen Storage

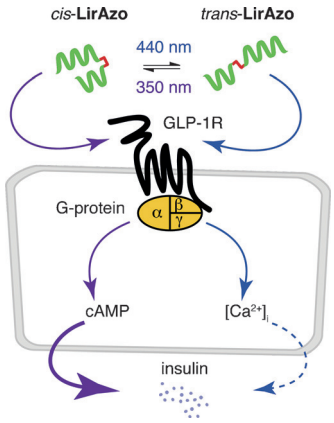


Two boron atoms collaborate: A highly efficient bis(borane) Lewis acid catalyst, which can be reused multiple times without loss of activity, catalyzes the release of 2.46 equivalents of H_2 per $H_3N–BH_3$ molecule. The dehydrogenation can be initiated and stopped on demand simply be heating to 60 °C or cooling to room temperature. Mechanistic studies provide insight into the mode of action of the catalyst.



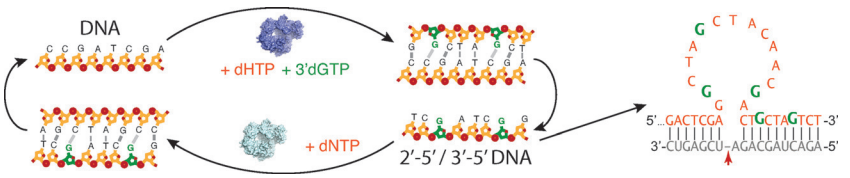
A terrestrial dive to bengamides: Bengamides, sponge-derived natural products, have been generated from a terrestrial source. Their biosynthesis and self-resistance mechanism against methionine aminopeptidases was elucidated, a heterologous expression platform was established, and their pharmaceutical properties were improved by medicinal chemistry.

Natural Products



Incretins in the spotlight: An azobenzene photoswitch was placed between the alpha helices of the incretin mimetic liraglutide to yield isomer-biased optical control over glucagon-like peptide-1 receptor (GLP-1R) signaling, pancreatic beta cell function, and insulin release.

Photopharmacology



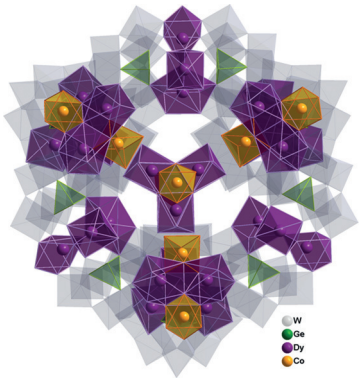
Specific distortion: A novel engineered polymerase can synthesize both DNA and RNA with regioisomeric 2′-5′ backbone linkages. It forms the basis for position-selective incorporation of 2′-5′ linkages enabling "structural mutagenesis". As a result structure, conformation, duplex stability, and activity of nucleic acids may be probed through the site-specific insertion of regioisomeric backbone distortions.

Nucleic Acid Modifications

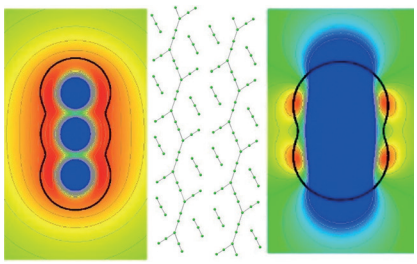
Polyoxometalates

Back Cover

Record SMM POM: A new class of polyoxometalate (POM) containing 3d–4f and 4f aggregates encapsulated by [*A*-α-GeW_9O_{34}]$^{10-}$ ligands to give $[Dy_{30}Co_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$ is described. This hybrid with single-molecule magnet (SMM) behavior contains the largest number of 4f ions of any POM reported to date and is the first to incorporate two different 3d–4f and 4f coordination cluster assemblies within same POM framework.



Cl–Cl Bonds



In a eutectic mixture of two ionic liquids, it was possible to synthesize and crystallize the new polychloride compound $[Et_4N]_2[(Cl_3)_2{\cdot}Cl_2]$. This new compound exhibits a periodic 2D polychloride network based on halogen–halogen interactions forming an anionic layer.

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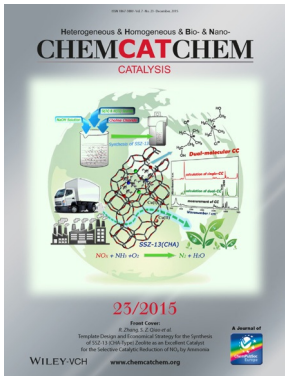

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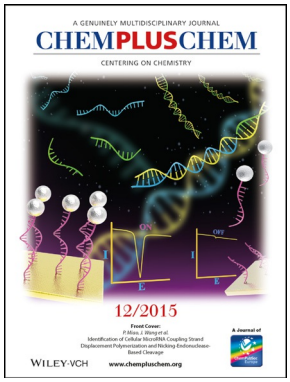

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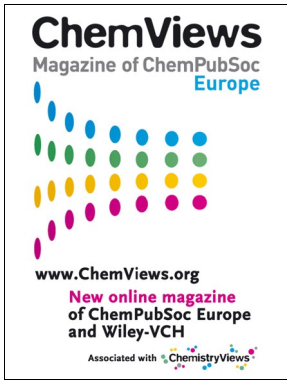

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