Editorial

"... France has a long-standing tradition of research and innovation in chemistry, and its chemical industry (ranked fifth in the world) is still a strong pillar of the French economic development ..."
Read more in the Editorial by Alain Fuchs.

Service

Author Profile

"Chemistry is fun because new findings raise my spirits. When I was eighteen I wanted to be either a mathematician or a chemist. ..."
This and more about Masahiro Miura can be found on page 12656.

News


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Books

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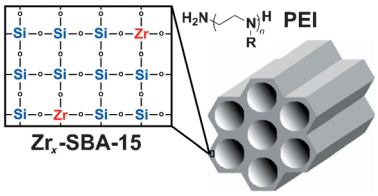
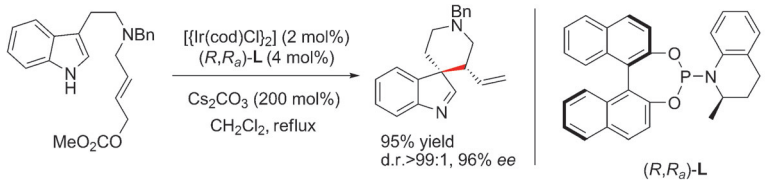
Highlights

Worth the wait: A new variable, zirconium content, has been added to the already complex amine-supported porous silica systems used for CO_2 capture. SBA-15 incorporating Zr ions and loaded with poly(ethyleneimine) was exposed to simulated flue gas (10% CO_2) and ambient air (400 ppm CO_2). Not only was the performance of the Zr-doped material significantly better than that of the pristine system, it also displayed improved desorption kinetics.



CO_2 Capture

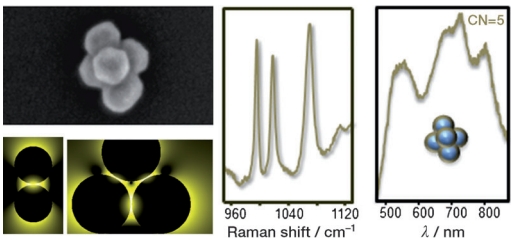
Reviews



Breaking up the party: Arenes can be transformed efficiently into enantiomerically enriched, versatile ring systems by catalytic asymmetric dearomatization reactions. Known reaction types include oxidative dearomatization, dearomatization by Diels—Alder reactions, alkylative dearomatization of electron-rich arenes, transition-metal-catalyzed dearomatization reactions (see example), and cascade reaction sequences involving asymmetric dearomatization as the key step.

Asymmetric Catalysis

Communications



Highly symmetric gold nanoparticle clusters with coordination numbers up to seven were produced by using coating with block copolymers. The resulting clusters were separated by density gradient centrifugation and characterized by using SEM and optical spectroscopy (see picture).

Nanoparticle Clusters

The German Chemical Society (GDCh) invites you to:

Angewandte Anniversary Symposium

125 JAHRE Eine Zeitschrift der Gesellschaft Deutscher Chemiker

GDCh

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

Speakers

Carolyn R. Bertozzi

François Diederich

Alois Fürstner

Roald Hoffmann (Nobel Prize 1981)

Susumu Kitagawa

Jean-Marie Lehn (Nobel Prize 1987)

E.W. "Bert" Meijer

Frank Schirrmacher (Publisher, *FAZ*)

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More information:

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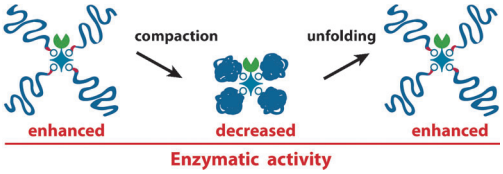
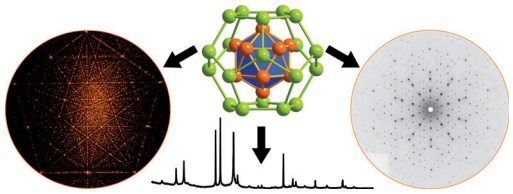


A giant DNA leap for enzyme-kind: Giant DNA–protein multibranch conjugates were shown to be composed of a single β-lactamase enzyme (green, see scheme) conjugated to up to four 48.5 kbp lambda phage DNA branches (blue lines). The conjugation of giant DNA induces a two- to fourfold enhancement of the enzymatic activity, which is modulated by changes in the higher-order DNA structure.

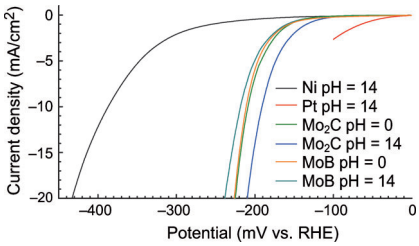
DNA–Enzyme Conjugates



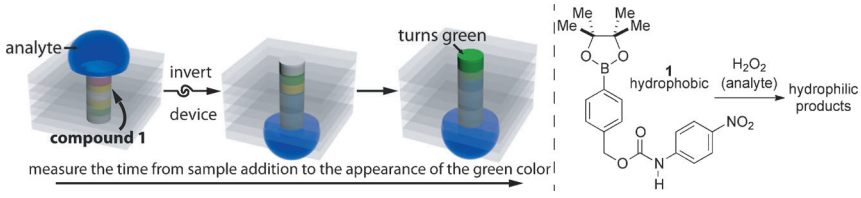
Golden opportunity: $Na_{13}Au_{12}Ga_{15}$ is the first Na-containing, thermodynamically stable quasicrystal and was discovered during systematic exploration of the polar intermetallic Na–Au–Ga system. Its electron-to-atom ratio, 1.75, is extremely low for Bergman-type icosahedral phases, but it is the substantial Au content that allows Hume–Rothery stabilization and promotes novel Na–Au polar–covalent interactions, which stabilize the icosahedral phase.

Intermetallic Phases

Getting the hydrogen out: Molybdenum boride (MoB) and carbide (Mo_2C) are excellent catalysts for electrochemical hydrogen evolution at both pH 0 and pH 14.

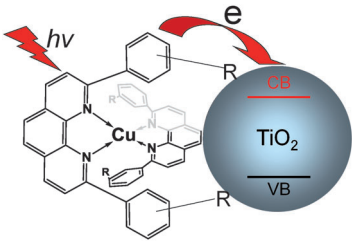


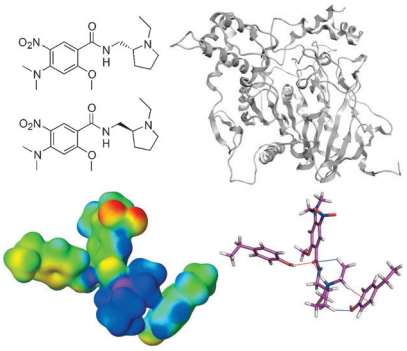
Water Splitting

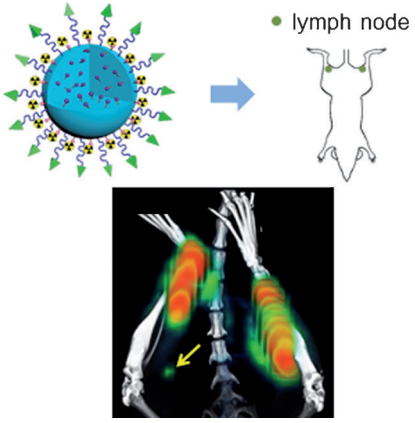


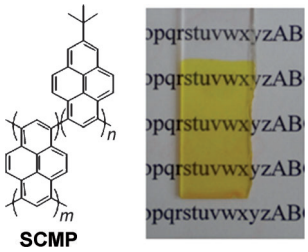
A matter of time: Two quantitative assays are presented that require only measurements of time and the ability to see and/or count to quantify the presence of a specific analyte. The strategies rely on specific changes in wetting properties of paper when a hydrophobic detection reagent (compound **1**) reacts with a desired analyte to produce hydrophilic products. This change in wetting properties enables selective and quantitative detection of the analyte.

Assay Development

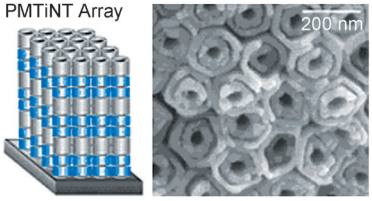




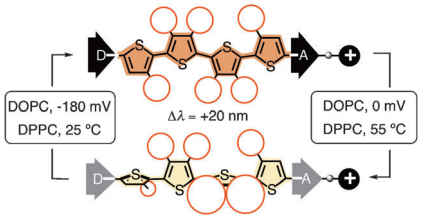




Cu–Pt bimetallic shells supported on a double-walled TiO_2 nanotube (PMTiNT) array are efficient photocatalysts for the room-temperature conversion of CO_2 into light hydrocarbons, such as CH_4, C_2H_4, and C_2H_6. When $Cu_{0.33}$–$Pt_{0.67}$/PMTiNT was used for the photoreduction of diluted CO_2 (1% in N_2), an average hydrocarbon production rate of 3.7 mL g^{-1} h^{-1} or 6.1 mmol m^{-2} h^{-1} was realized under AM 1.5 one-sun illumination.



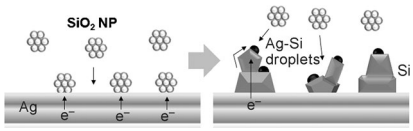
CO_2 Photoreduction



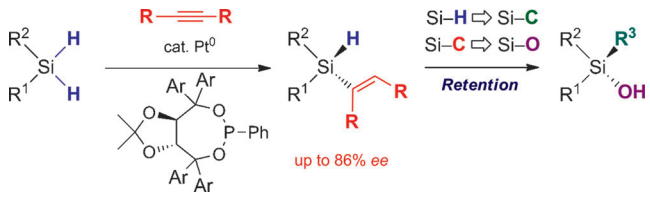
Lessons from lobster coloration and the chemistry of vision suggested an approach to responsive fluorescent probes that can sense membrane potential, fluidity, and tension. Fluorophore deplanarization by lateral crowding along the scaffold (red circles) and fluorophore polarization by terminal donors (D), acceptors (A), and charges (+) are coupled to provide such membrane probes, as studies with unilamellar vesicles of phospholipids (DOPC, DPPC) show.

Fluorescent Probes

Silicon for solar cells: Relatively pure, polycrystalline, and photoactive silicon was directly obtained from silicon dioxide nanoparticles (NP) by electrodeposition in molten $CaCl_2$ salt on a silver electrode (see picture). This process is based on the formation of liquid droplets of a silver–silicon eutectic alloy and the continuous reduction of SiO_2 to silicon. The deposited silicon shows a p-type behavior in photoelectrochemical measurements.



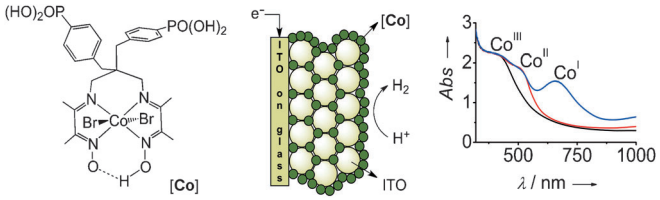
Electrochemistry



Asymmetric silanes: A synthesis of nonracemic alkenylhydrosilanes has been developed based on the desymmetrization of a dihydrosilane through alkenylation with an alkyne using an asymmetric catalyst. The alkenylhydrosilane product can be used as a versatile chiral building block for other functionalized nonracemic silanes through the stereoselective conversion of its hydride and/or alkenyl moiety.

Chiral Silanes

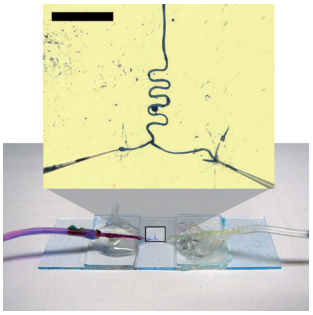
Hybrid Materials



Energizing Cobalt on a 3D Electrode: An optically transparent mesoporous ITO film was derivatized with the novel proton reducing cobalt catalyst [**Co**]. The hybrid electrode showed high current densities, and spectroelectrochemical studies and extensive surface characterization demonstrate that the immobilized molecular catalyst remained intact on the electrode when applying a low potential.

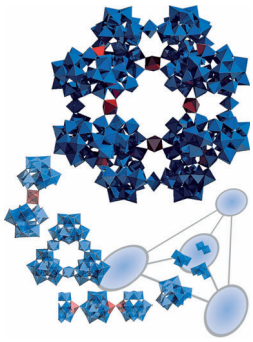
Polyoxometalates

Go with the flow: Laser-induced flow patterns are used to direct the self-assembly of dissolved inorganic polyoxometalate clusters into robust, hollow tubular networks and micro-materials (see picture; scale bar: 500 μm) in real time. The hollow nature of these materials can be exploited to develop devices in which the self-assembled tubes act as microscopic flow channels.



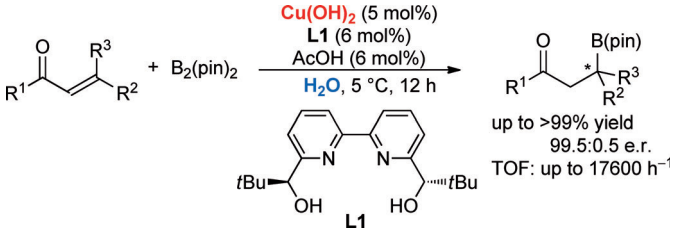
Front Cover

Polyoxometalates

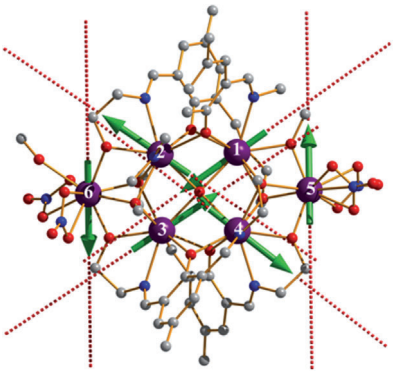


A giant leap: A networked reactor system was used for the first time for the discovery and synthesis of new polyoxometalates, including the gigantic title system (see picture; Co red, W blue). The system comprises of three reactors connected in a triangular array with a central triply connected reactor. This system was used to screen multiple one-pot reactions and reaction variables for the automated syntheses of polyoxometalates.

Asymmetric Catalysis

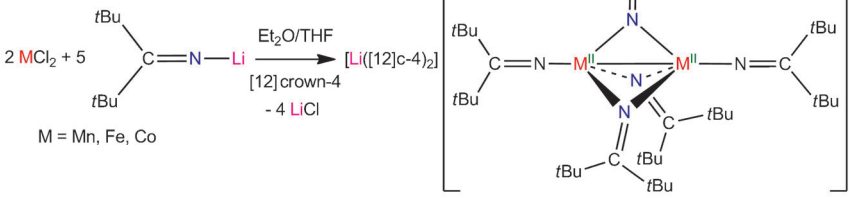


Copper pins on the boron: The enantioselective 1,4-addition of diboron to α,β-unsaturated compounds proceeds smoothly in the presence of catalytic amounts of $Cu(OH)_2$ and chiral 2,2′-bipyridine ligand in water. A wide substrate scope of α,β-unsaturated carbonyl compounds, including acyclic, cyclic, and β,β-disubstituted enones, α,β-unsaturated esters, amides, and a nitrile, has been shown.



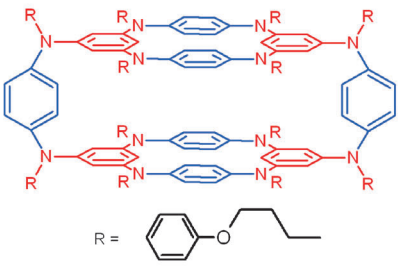
A hexanuclear dysprosium(III) compound constructed by two Dy_3 triangles in an edge-to-edge arrangement perfectly retains a nonmagnetic ground state and single-molecular-magnet behavior. Such an arrangement and the strong couplings over a μ_4-O^{2-} ion stabilize a similar arrangement of toroidal moments in the ground state, thus maximizing the toroidal moment of the complex. (Picture: Dy purple, C gray, N blue, O red.)

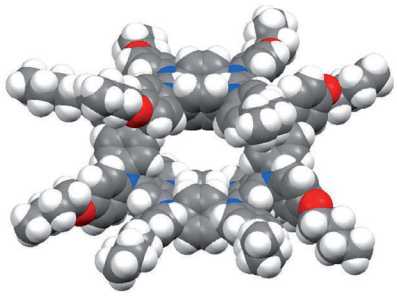
Single-Molecule Magnets



Bond, metal–metal bond: Addition of 2.5 equiv of $Li(N{=}CtBu_2)$ to MCl_2 (M = Mn, Fe, and Co), followed by addition of [12]crown-4, results in formation of $[Li([12]crown\text{-}4)_2][M_2(N{=}CtBu_2)_5]$ in good yields. These complexes exhibit short M–M distances and strong magnetic communication between metal centers, thus demonstrating that ketimides are viable co-ligands for promoting metal–metal bonding.

Metal Ketimides

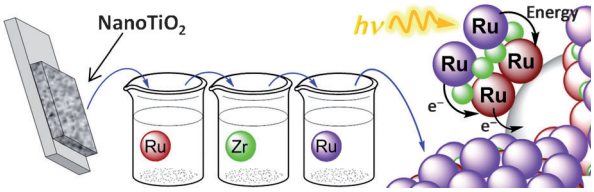




Spin doctor: The polymacrocyclic oligoarylamine in the picture serves as a multispin source owing to its multi-electron redox activity. As a result of its pseudobeltane structure and *para*-phenylenediamine bridges, the radical cation can convert between two sideslipped structures with a windshield-wiper-like motion. In contrast, the tetraazacyclophane units are rigid components in the polymacrocycle.

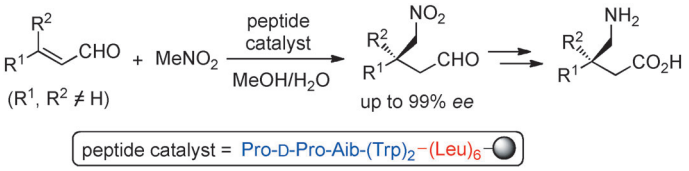
Cyclophanes

Electron Transfer



Simple assembly: A "layer-by-layer" deposition of functionalized dyes/catalysts on the surfaces of nanocrystalline oxides is introduced. The strategy is general and offers considerable flexibility based on phosphonate- or carboxylate-binding groups with Zr^{IV} as bridging ions. The resulting bilayer structures are capable of supporting rapid intra-layer energy and electron transfer (see picture).

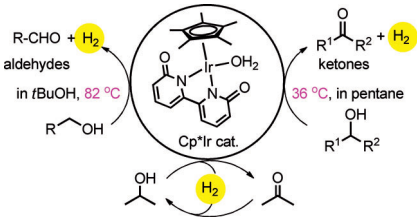
Peptide Catalysis



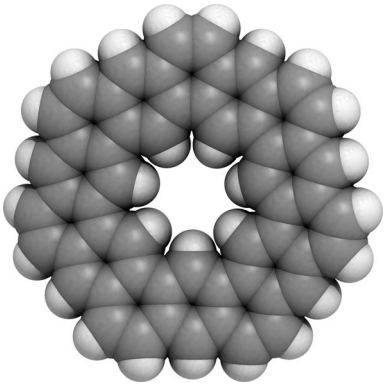
Pepping up Michael: An asymmetric Michael addition of nitromethane to β-disubstituted α,β-unsaturated aldehydes was realized by a resin-supported peptide catalyst. Whereas the use of a low-molecular-weight catalyst resulted in poor yields, the peptide effectively promoted the reaction in aqueous media with high enantioselectivity.

Dehydrogenation

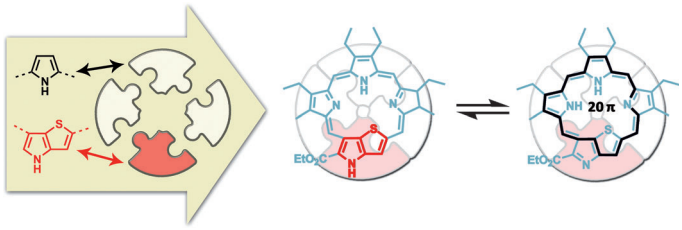
Going into reverse: An efficient and versatile catalytic system for the dehydrogenative oxidation of alcohols under extremely mild conditions has been developed using a Cp*Ir complex with bipyridonate ligand as catalyst (see scheme, Cp* = pentamethylcyclopentadienyl). Reversible and repetitive transformation between 2-propanol and acetone by catalytic dehydrogenation–hydrogenation is also achieved.



Kekulene

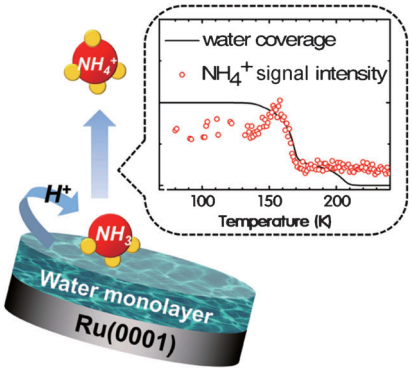


A family likeness: The seven-sided homologue of kekulene, septulene (see structure), has been synthesized in seven steps by ring-closing metathesis. Its properties (spectroscopic and structural) are strikingly similar to those of kekulene despite its sevenfold symmetry and resulting non-alternant structure. The chair-type conformation in the crystal arises from packing forces. Septulene is probably a free pseudorotor in the gas phase.



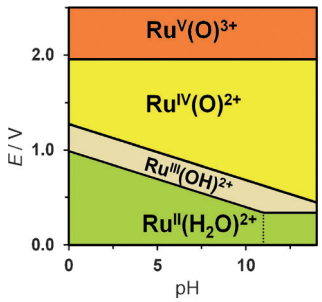
Easy as π: A stable nonaromatic heteroporphyrin bearing a thienopyrrole moiety has been prepared. The nonaromatic nature of this compound is clearly evident based on UV/Vis absorption, ^{1}H NMR spectroscopy, and theoretical calculations. Single-crystal X-ray analysis demonstrates that the molecule adopts a planar conformation with clear alternation in the C–C bond lengths around the periphery of the macrocycle.

Porphyrinoids



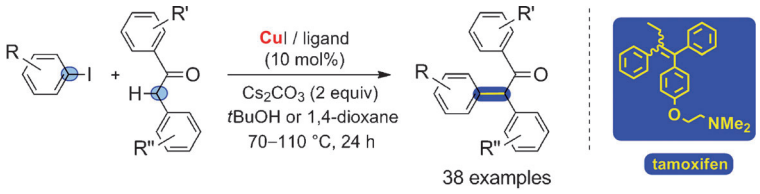
Acidic water: The first monolayer of water on a Ru(0001) surface is anomalously acidic compared to bulk water, according to infrared and mass spectroscopic investigations of the water layer using ammonia as a probe for surface acidity. The observation suggests that acid–base chemistry may be quite different at the water–metal interfaces than in aqueous solution.

Water–Solid Interfaces



We can do better! The new density functionals M11-L and M11 and the SMD implicit solvation model were used to predict reduction potential–pH equilibrium diagrams (see example) for two ruthenium-based water-oxidation catalysts and their derivatives in aqueous solution. The observed improved accuracy for transition-metal complexes opens new opportunities for the use of theory in the understanding and design of catalysts containing transition metals.

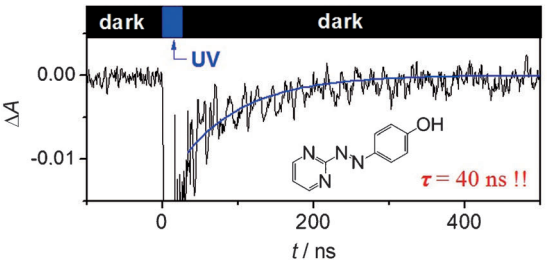
Computational Electrochemistry

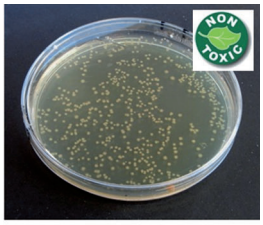


No activation needed: The first efficient method for direct α-arylation of non-activated or non-protected family of enolizable ketones with simple aryl iodides employs a catalytic copper system. The method shows potential for the easy and step-economical synthesis of tamoxifen, the most commonly administrated drug for the management of breast cancer. R, R′, R″ = electron-donating or electron-withdrawing groups.

Synthetic Methods

Fast Photoswitches

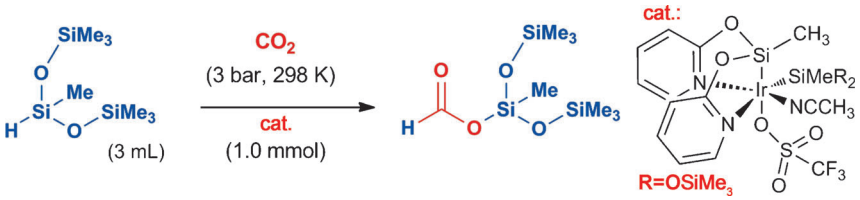




E. coli

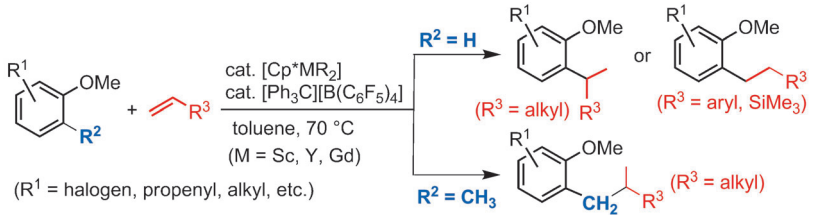
When speed is of the essence: After photoisomerization to its metastable *cis* form, an azo dye must undergo fast thermal isomerization back to the *trans* form to be suitable for real-time information transmission. The azopyrimidine shown has a relaxation time (τ) of just 40 ns under physiological conditions, as well as high biocompatibility, as determined by *Escherichia coli* growth in its presence (see picture).

CO_2 Hydrosilylation



CO_2 as feedstock: An air- and moisture-stable iridium(III) catalyst effectively promotes the hydrosilylation of CO_2. This reaction leads to silyl formate in a highly selective manner and proceeds efficiently under mild conditions, most likely by an outer-sphere mechanism, as suggested by theoretical calculations.

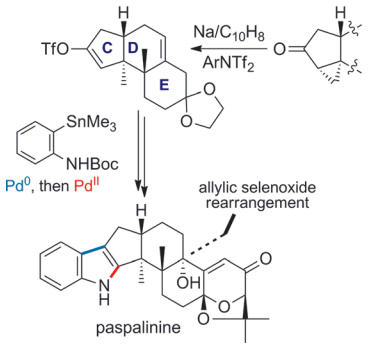
C–H Alkylation

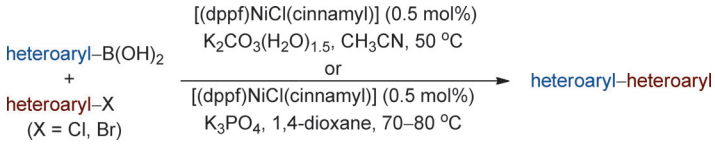


A half sandwich helping: Cationic rare-earth alkyl species generated from half-sandwich rare-earth dialkyl complexes and $[Ph_3C][B(C_6F_5)_4]$ can serve as unique catalysts for the C–H regioselective alkylation of anisoles with alkenes. The reaction affords either *ortho*-monoalkylated derivatives or products substituted at the benzylic position, depending on the substrate chosen.

Natural Product Synthesis

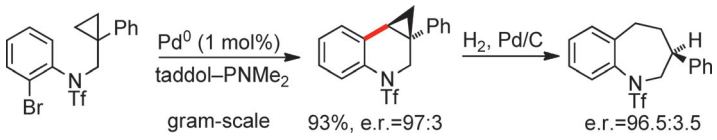
Succinct and stereoselective: A high-yielding two-step indole ring installation comprising the Stille cross-coupling and a Pd^{II}-mediated oxidative heterocyclization was exploited in a concise total synthesis of paspalinine. The *trans-anti-trans* CDE fused ring system of the heptacyclic natural product was established highly stereoselectively through hydroxy-directed cyclopropanation and allylic selenoxide rearrangement.





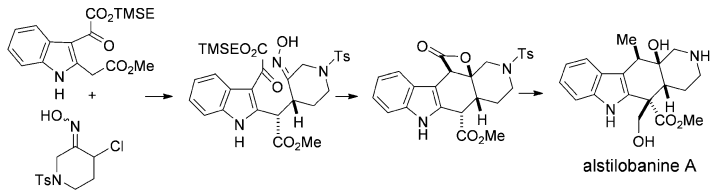
One for all: The coupling of a range of nitrogen- and sulfur-containing heteroaryl halides with five-membered nitrogen-, oxygen-, and sulfur-containing heteroaryl boronic acids were achieved in high yields with only 0.5 mol% of the single-component nickel precatalyst [(dppf)NiCl(cinnamyl)] (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene). The reaction demonstrates good functional group compatibility, and is easily conducted on a large scale without a dry box.

Heterobiaryl Cross-Coupling



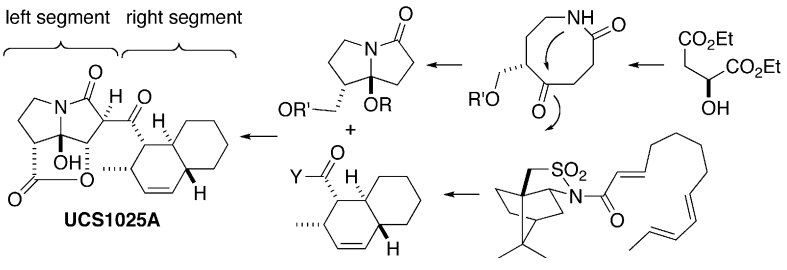
Activated: The title reaction proceeds efficiently with 1 mol% of palladium and gives tetrahydroquinolines in excellent enantioselectivities (see scheme). The enantiodiscriminating concerted metalation–deprotonation step occurs via a rare seven-membered palladacycle. The cyclopropyl-substituted tetrahydroquinolines can be regioselectively and enantiospecifically reduced to chiral tetrahydrobenzoazepines.

C–H Activation



Tetracyclic monoterpene alkaloid alstilobanine A was obtained in racemic form. The pivotal steps of the total synthesis are a novel conjugate addition of an ester enolate with a nitrosoalkene, as well as a formal [2+2] intramolecular cycloaddition leading to a β-lactone to generate the requisite *cis*-fused 2-azadecalin moiety of the alkaloid. TMSE = trimethylsilylethoxy, Ts = 4-toluenesulfonyl.

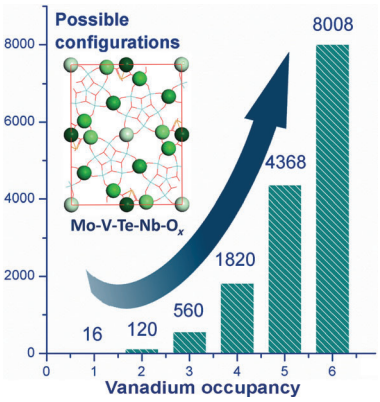
Natural Product Synthesis



Under control: A stereocontrolled total synthesis of (+)-UCS1025A, a potent telomerase inhibitor, was achieved. The synthesis features an intramolecular Diels–Alder reaction, a tandem Staudinger/aza-Wittig reaction, and stereoselective construction of the hemiaminal moiety facilitated by neighboring-group participation.

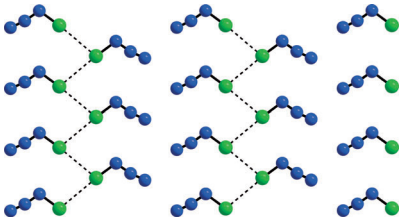
Natural Product

Multicomponent Oxide Catalysts



A V V good idea: The V occupancy (shown as a scale of green in the picture) and V–V pair probability in a Mo-V-Te-Nb mixed oxide were determined by weighted average over all possible (up to 8000) configurations on the basis of estimated DFT energies, which agreed well with those obtained by full optimization ($R^2 > 0.94$, maximum error below 0.05 eV). This rapid approach provided insight into the origin of the catalytic activity of these solids.

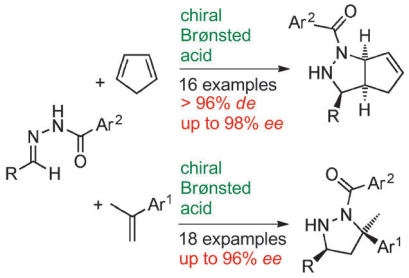
Halogen Azides



Delicate crystals: ClN_3 adopts a polymeric structure in the solid state (see picture; N blue, Cl green) with short intermolecular Cl···Cl distances, as was observed for the elemental halogen.

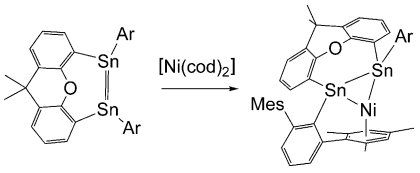
Organocatalysis

A general, metal-free, highly enantioselective Brønsted acid catalyzed [3+2] cycloaddition between hydrazones and alkenes has been developed that affords pyrazolidine derivatives (see scheme). The resulting optically active pyrazolidines can undergo many chemical transformations which allow, for example, the enantioselective synthesis of valuable pyrazolines and 1,3-diamines.

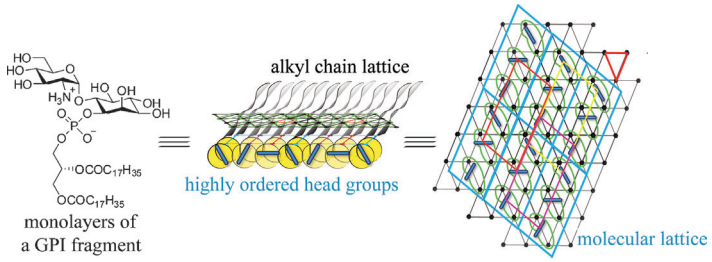


Coordination Chemistry

η^2-coordination of a Sn–Sn bond: An intramolecular distannene was synthesized in a straightforward fashion from 4,5-dilithio-9,9-dimethylxanthene. This compound reacts with $[Ni(cod)_2]$ to form a Ni^0 complex with an unprecedented Sn_2Ni triangle (see scheme; cod = 1,5-cyclooctadiene).

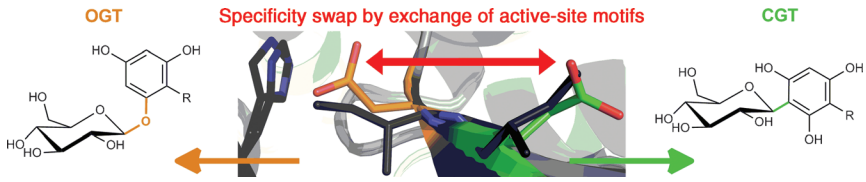


Ar = C_6H_3-2,6-Mes_2, Mes = C_6H_2-2,4,6-Me_3



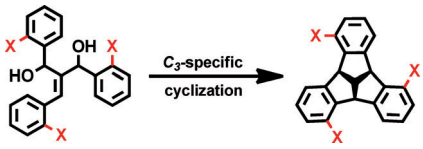
Heads and tails: GPI glycolipid monolayers on the air/liquid interface are characterized by the ordering of entire molecules, as observed by grazing-incidence X-ray diffraction. Strong hydrogen bonding interactions are responsible for ordering of the head groups to form supercells. These forces are likely to be the key to the interactions of GPI-anchored proteins and/or GPIs in cell membranes.

Glycophospholipid Monolayers



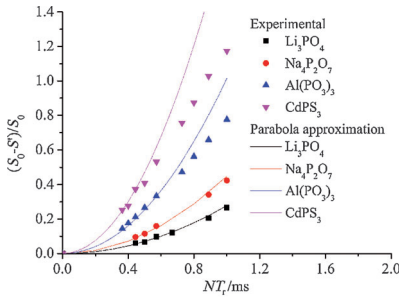
Mechanistic implications: Distinct active-site motifs in plant aryl glucosyltransferases of the GT-1 family differentiate between *C*- and *O*-glycosylation activity on a phloretin acceptor. In the implicated protein design principle the exchange of active-site motifs results in reversible switch between *C*/*O*-glycoside specificity. The proposed mechanism of the *C*-glycosyltransferase involves direct nucleophilic displacement at the anomeric carbon.

Enzyme Mechanisms



Fusing rings: A new synthesis of the bowl-shaped hydrocarbon tribenzotriquinacene is presented (see scheme). The synthesis allows easy access to *ortho*-functionalized and C_3-chiral derivatives that are attractive for supramolecular chemistry and asymmetric catalysis.

Bowl-Shaped Molecules

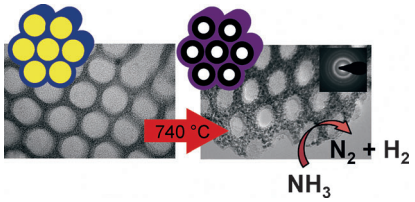


In a new solid-state NMR method a double-quantum Hamiltonian based on a POST-C7 pulse sequence is used to recouple the homonuclear dipole–dipole interactions. Similar to the heteronuclear rotational echo double-resonance (REDOR) method, an analysis of the difference signal at short evolution times yields site-resolved summed squares of the dipole–dipole coupling constants.

NMR Spectroscopy

Ordered Carbides

Hexagonally ordered mesoporous molybdenum oxycarbide/carbon (MoC/C) nanocomposites were directly accessed by heat treatment of mesostructured poly(butadiene-*block*-2-vinylpyridine) (PB-b-P2VP) and molybdophosphoric acid. PB-b-P2VP serves as structure-directing agent and as carbon source. The high specific surface area obtained for the nanocomposites renders the materials interesting for potential applications, such as in the catalytic decomposition of NH_3.



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