VIP The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

Author Profile

"If I were not a scientist, I would be a chef or sommelier. My favorite place on earth is the summit of any mountain …"
This and more about Warren E. Piers can be found on page 3514.

News


D. Milstein


R. Shintani


H. Schwarz


S. Hell

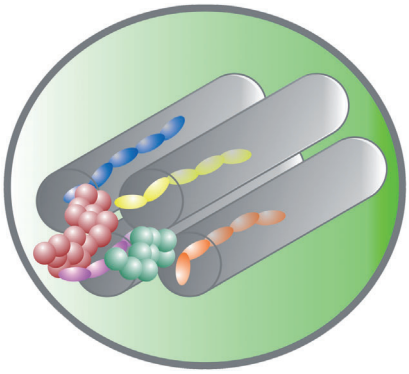

P. Schwille

Books

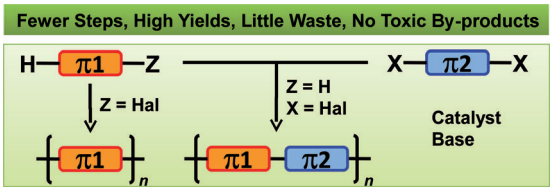
Highlights

Mesoporous Materials

Peptide profiles: The use of mesoporous materials, such as ordered mesoporous carbon, improves the efficiency and selectivity of peptide extraction for profiling complicated samples. Controling the pore size of such mesoporous materials during synthesis allows specific molecular weight cut-offs to be introduced, which can eliminate a large number of interfering entities, such as serum proteins.



π-Conjugated Polymers

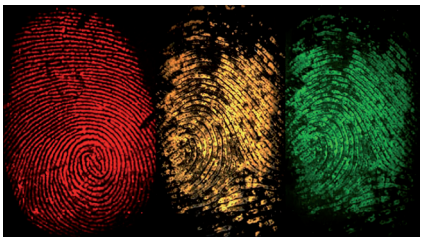


Two flavors of π: Semiconducting π-conjugated polymers may open new opportunities for the fabrication of ecofriendly, inexpensive optoelectronic devices. These materials can be prepared by direct arylation polycondensation, a straightforward approach that generates little waste and no toxic by-products.

Minireviews

Fingerprinting

Reading the small print: The detection of analytes of forensic importance such as drugs of abuse and explosives from a person's fingerprint together with the ability to identify that person is an important development in forensic science. This Minireview highlights the advances in this area of research, such as the use of nanoparticles, magnetic particles, quantum dots, as well as mass spectrometry, and spectroscopy.



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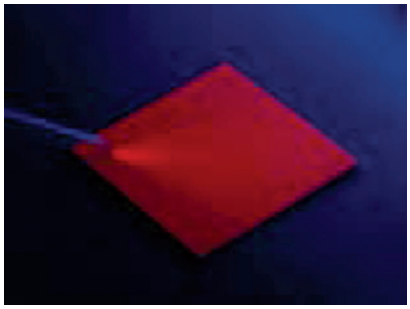
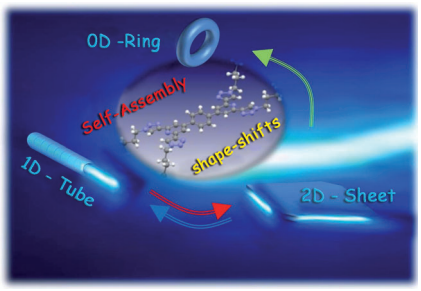
Reviews

The art of sensorship: Fluorescence imaging methods in combination with optical chemical sensors enable the visualization of flows on surfaces (see picture), temperature gradients, and the two-dimensional distribution of certain chemical species (O_2, H^+, metal ions, H_2O_2) at an interface. This Review highlights the design of sensor materials, including nanoprobes, and the development of multiple sensors and their signal readout.

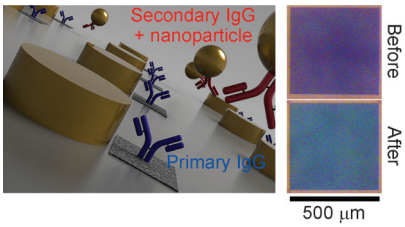


Communications

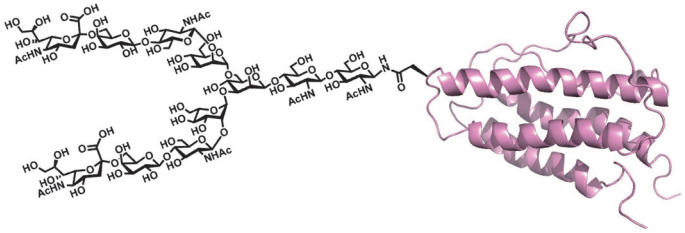


Shape-shifting: A method for reversibly transforming the shape of organic waveguides to form 2D nanosheets, 1D nanotubes, and 0D nanorings has been developed. The nanosheets can be turned into nanotubes and subsequently into nanorings by adding water to the solvent, whereas ultrasonication changes the nanotubes back into nanosheets. Both nanotubes and nanosheets act as waveguides and change the direction of incident laser light in a shape-dependent manner.

Naked-eye detection: The versatility of direct-write nanolithography was combined with the unrivaled resolution and selectivity of molecular self-assembly to show, for the first time, the molecularly mediated placement, with nanometer accuracy, of single Au nanoparticles within a plasmonic array. In doing so, a coupled plasmonic systems was created which allowed colorimetric, naked-eye detection of protein–protein binding at extreme sensitivities.



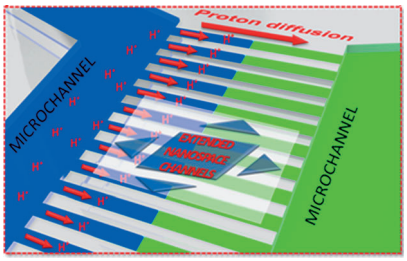
Glycoprotein Synthesis



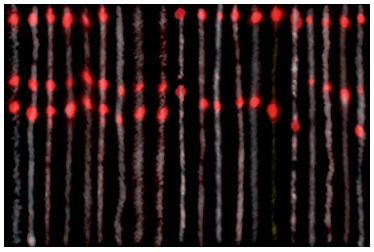
New and improved: New reaction conditions for *tert*-Boc-based solid-phase peptide synthesis make acid-labile sialyloligosaccharyl peptide α-thioesters accessible. To demonstrate this, a sialyloligosaccharyl-erythropoietin glycoform (see picture) with 166 amino acid residues was synthesized.

Proton Mobility

Channeling of mobility: A new method for the direct measurement of proton mobilities based on a pH-sensitive fluorescence probe is described. The results verify the enhancement of proton mobility in two-dimensional extended nanospace channels and contribute to a deeper understanding of ion-transport processes inside nanochannels.

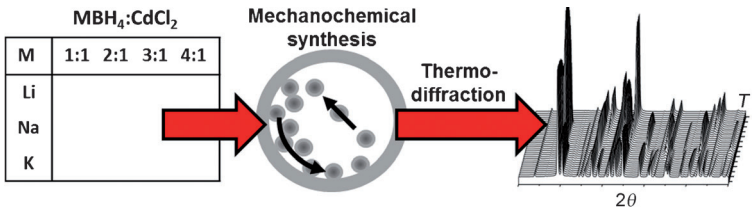


Genomic Imaging



All smiles: Sequence-specific methyltransferase-induced labeling of DNA (SMILing DNA) creates a fluorescence pattern of the T7 bacteriophage genome (see picture). The pattern is visualized as a linear optical barcode showing the genomic location of individual RNA polymerases bound to the DNA. The precision of the measurement presents new opportunities for contextual genomic research on the single-molecule level.

Unstable Borohydrides

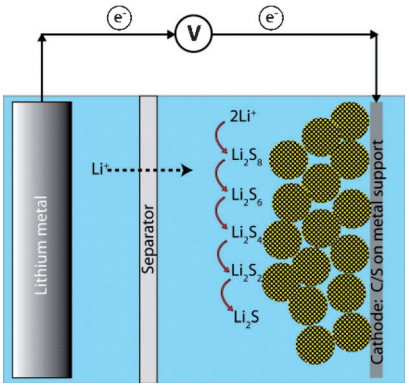


Ay, there's the rub: The formation of cadmium-based borohydrides is screened by mechanochemical synthesis using various reactants in different ratios. Sequential in situ variable-temperature diffraction studies provide simultaneous information about composition, structure, decomposition pathways, and properties of the compounds.

Rattling the cage: The rapid one-pot double 1,3-dipolar cycloaddition reaction of the rare endohedral fullerene N@C_{60} to an oligo(*p*-phenylene polyethylene) bis-(aldehyde) using a novel amino acid derivative as an anchoring group is reported. The method provides the first example of a chemically linked, two-spin-center N@C_{60}–N@C_{60} molecule (see picture). Assessment of this platform as an element of a quantum computing register is attractive.

Cage Compounds

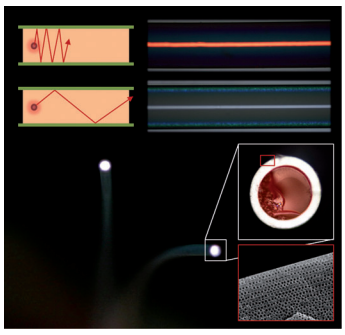
Superior cathode material: Spherical ordered mesoporous carbon nanoparticles featuring very high inner porosity (pore volume of 2.32 $cm^3 g^{-1}$ and surface area of 2445 $m^2 g^{-1}$) were synthesized in a two-step casting process. They were successfully applied as cathode material in Li-S batteries, where they showed high reversible capacity up to 1200 $mA h g^{-1}$ and excellent cycling efficiency.



Lithium–Sulfur Battery

Squeezing out the energy: Macroscopically reversible deformation of polymers in contact with water produces H_2O_2 in quantities that are sufficient to drive small-scale chemical syntheses. The amount of mechanosynthesized H_2O_2 scales with the polymer–water interfacial area, and the efficiency of the mechanical-to-chemical energy transduction can be as high as 30% for soft, porous polymer "sponges".

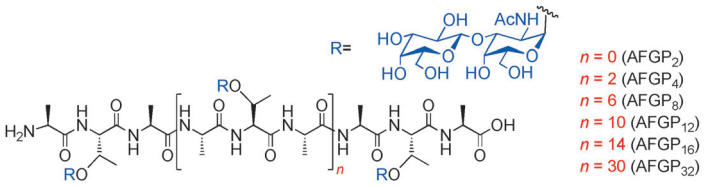
Mechanochemistry



Photonic crystal fibers have been created using the spontaneous crystallization of colloidal particles in a photocurable resin coated on the inner wall of microcapillaries. The controlled deposition of films on the microcapillaries allows the thickness and number of layers in the photonic crystal fibers to be controlled. A stop band in a colloidal photonic crystal fiber can enhance the efficiency of light guidance (see picture).

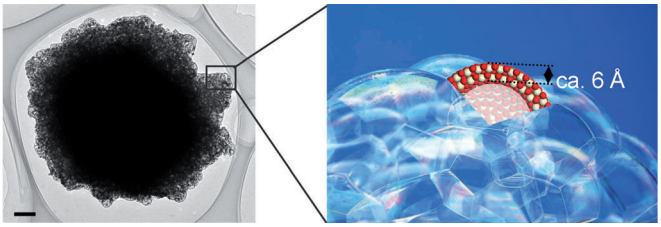
Photonic Crystals

Peptide Ligations



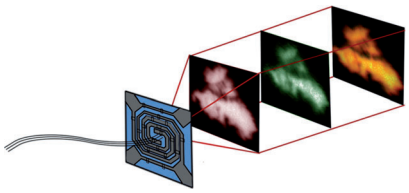
Don't freeze! A native chemical ligation–desulfurization strategy has been employed for the convergent synthesis of a library of defined antifreeze glycopeptides and glycoproteins (AFGPs) ranging in size from 1.2 to 19.5 kDa (see picture). These AFGPs possessed the secondary structure of a polyproline type II helix and exhibited significant ice recrystallization inhibition and thermal hysteresis activity.

Ceria Foams



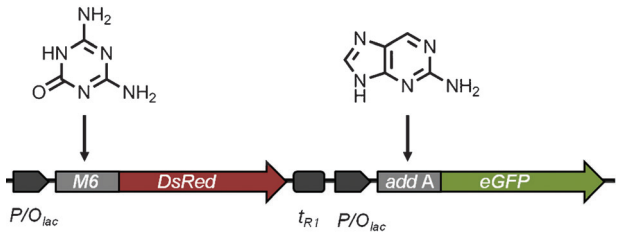
All in a lather: A three-dimensional CeO_2 foam with long-range ultrathin (4–8 Å) single-crystalline walls was synthesized successfully by thermal decomposing $CeGeO_4$ crystals under an NH_3 atmosphere. First-principles calculations were also performed to understand the feasibility and reaction pathways of thermal decomposition of $CeGeO_4$. Scale bar: 200 nm.

Zeolite Catalysis

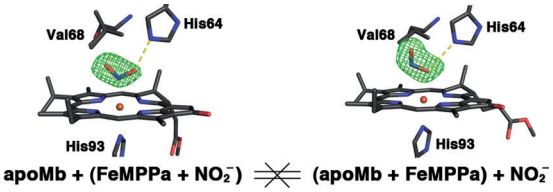


Zeolites in the spotlight: A combination of scanning transmission X-ray microscopy (see picture) and bulk methods give nanoscale chemical insight in the distribution of Al and C within ZSM-5 zeolites during methanol-to-olefin reactions. The distinct catalyst performances could be related to differences in the spatial distribution of the hydrocarbons.

Riboswitches

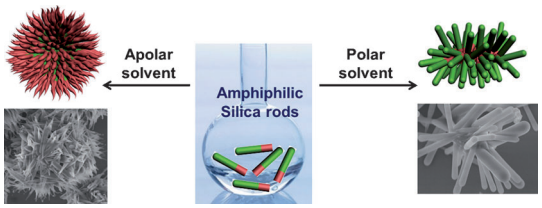


Orthogonal gene control: Orthogonal riboswitches can be deployed in the same bacterial cell to independently control the coexpression of multiple genes in a dose-dependent response to distinct synthetic small molecules. This technique allows convenient access to highly dynamic expression landscapes and desirable protein stoichiometries.



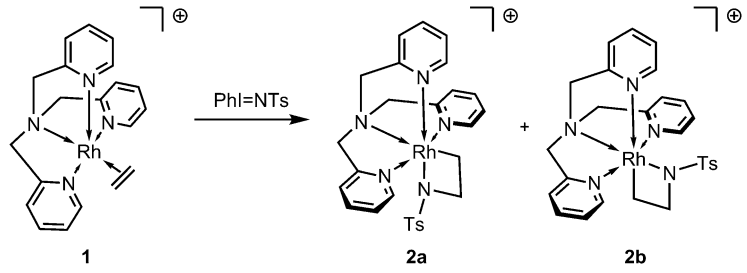
Who is in charge? Nitrite linkage isomerism in the same heme protein occurs as a function of the compound preparation method. An N-bound nitrite conformation is achieved when a pre-formed iron chlorin–nitrite model compound is inserted into apoMb. In contrast, an O-bound nitrite conformation is evident when nitrite is added to the chlorin-substituted Mb. The results suggest that the Mb distal pocket is in charge of directing the ligand binding mode.

Linkage Isomerism



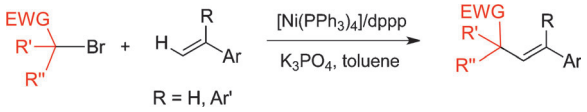
Flowers and stars: A wet-chemical method was developed to synthesize amphiphilic rodlike silica particles with hydrophilic (green in picture) and hydrophobic (red) blocks. The self-assembly of the amphiphilic rodlike particles leads to various structures including planar monolayers, bundle micelles, flower micelles, star micelles (right in picture), and reverse micelles (left) depending on the properties of the rods and the nature of the solvent.

Colloidal Particles



AmAZAing metallacycles: Azarhodacyclobutane was prepared by oxidation of Rh^{I}–olefin complex **1** (see Scheme; Ts = *p*-toluenesulfonyl). Both isomers **2a** and **2b** were isolated and characterized by NMR spectroscopy and mass spectrometry; their configurations were unambiguously established by NOE experiments.

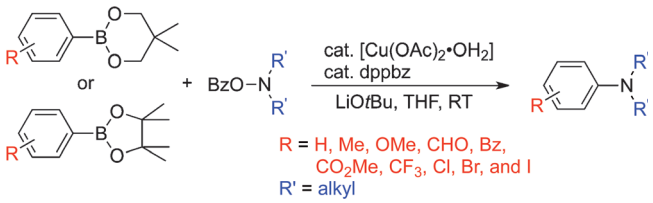
Metallacyclobutanes



Ni made it! A novel Heck-type reaction of secondary and tertiary α-carbonyl alkyl bromides, most likely involving a radical process, was achieved through the use of a nickel catalyst. Various substituted styrenes and 1,1-diaryl alkenes were utilized as substrates to easily construct α-alkenyl carbonyl compounds with tertiary or quaternary carbon centers. A catalytic cycle involving Ni^{I}/Ni^{II} is proposed based on our experimental results. EWG = electron-withdrawing group.

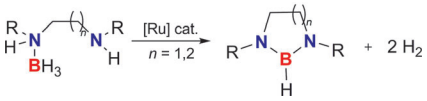
Cross-Coupling

Synthetic Methods



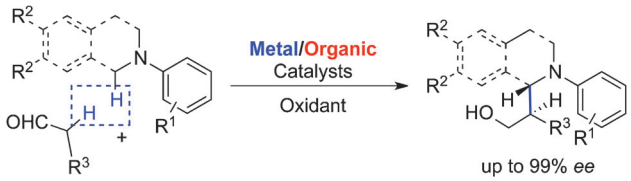
A tolerant coupling: The title reaction has been developed to deliver arylamines (see scheme; Bz = benzoyl, dppbz = 1,2-bis-(diphenylphosphino)benzene). The catalysis is based on electrophilic, umpolung amination and enables the use of secondary acyclic amines. Various functional groups are tolerated, thus opening up a new substrate class for the Chan–Lam-type coupling.

Homogeneous Catalysis



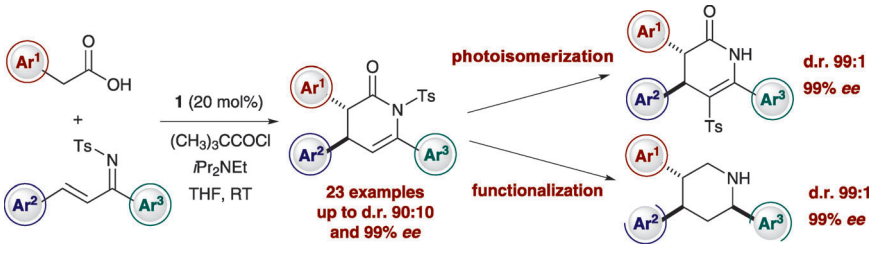
Remote control: The title reaction is the first example of a catalyzed dehydrogenative cyclization (CDC) of diamine–monoboranes to give cyclic diaminoboranes. The cyclization reaction is strongly dependent on the nature of the substitution pattern at the remote amino group.

Synthetic Methods

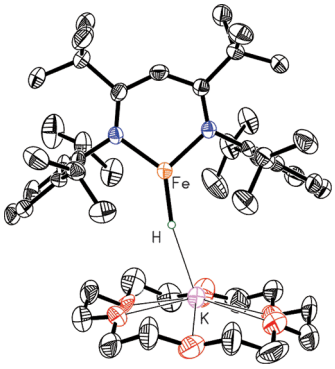


Cooperative catalysts: An enantioselective and direct oxidative coupling of aldehydes to tertiary amines to give β-amino alcohols is described. Catalyzed by copper(II), the reaction proceeds to give a racemic mixture of products; however, by using a combination of copper(II) and a chiral amine catalyst, the reaction gives the desired products with high enantioselectivity (see scheme).

Asymmetric Catalysis

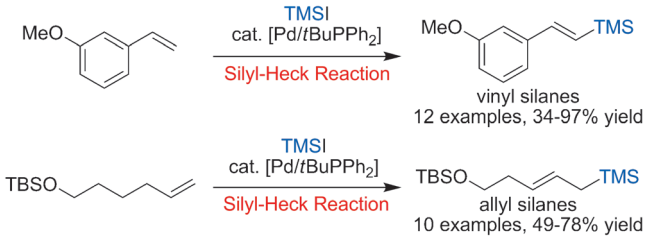


Benzotetramisole (1) promotes the reaction of ammonium enolates derived from arylacetic acids with *N*-tosyl-α,β-unsaturated ketimines, thus giving dihydropyridones with high diastereo- and enantiocontrol (see scheme). These products readily undergo N- to C-sulfonyl photoisomerization and are derivatized to afford stereodefined piperidines and tetrahydropyrans.



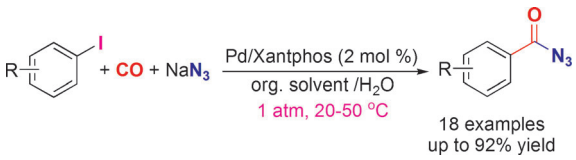
Three's company: Iron(I) hydride complexes are presented (see picture; N blue, O red) that are the first monomeric open-shell hydride complexes to be crystallographically verified as being three-coordinate at the metal. Backbonding into diketiminate π^* orbitals stabilizes the low oxidation state. The Fe–H bonding has been analyzed using electron-nuclear double resonance (ENDOR).

Hydrides in Biology



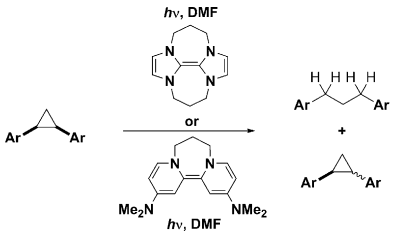
Installing silicon is easy! A high-yielding protocol for the palladium-catalyzed silylation of terminal alkenes is reported. This method allows facile conversion of styrenes to *E*-β-silyl styrenes by using iodotrimethylsilane (TMSI) or chlorotrimethylsilane/lithium iodide (see scheme). Terminal allyl silanes with good *E*/*Z* ratios are also readily accessed from α-olefins.

Synthetic Methods



Aryl iodides smoothly react with NaN_3 and CO in the presence of a Pd/Xantphos catalyst to give aroyl azides ($ArCON_3$) in 75–92% yield. The reaction occurs under mild reaction conditions (1 atm, 20–50 °C) and exhibits high functional-group tolerance. (Xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene)

Azidocarbonylation

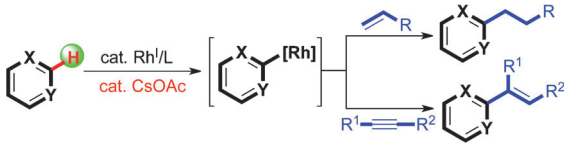


Powerful reduction reactions: Simple organic electron donors, composed solely of the elements carbon, hydrogen, and nitrogen, reduce ground-state benzene rings to their radical anions by electron transfer upon photoactivation (DMF = dimethylformamide).

Reduction of Benzenes

Hydroheteroarylation

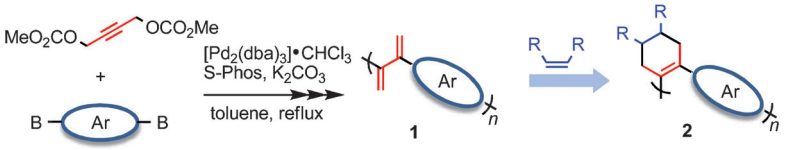
A Versatile Rhodium(I) Catalyst System for the Addition of Heteroarenes to both Alkenes and Alkynes by a C–H Bond Activation



Rhod to Addition: A highly efficient and convenient rhodium catalyst system was developed for the title transformation. A base co-catalyst was found to facilitate the key arene C–H bond-activation step and substrate scope was very broad, including both electron-deficient pyridine *N*-oxides, and electron-rich azoles. The catalytic system was effective for the hydroheteroarylation of both alkenes and alkynes and gave excellent regio- and stereoselectivity.

Polymerization

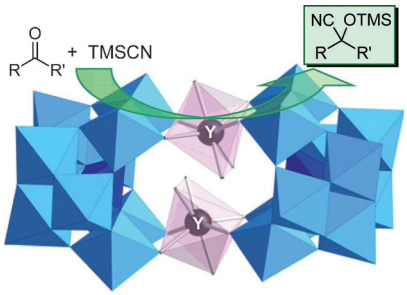
Palladium(0)-Catalyzed Synthesis of Cross-Conjugated Polymers: Transformation into Linear-Conjugated Polymers through the Diels–Alder Reaction



Making the shift: The title reaction of a propargylic bis(carbonate) with diboron compounds leads to new cross-conjugated polymers **1** having 2,3-butadienylene moieties. **1** is then converted into the linear-conjugated polymers **2** through a Diels–Alder reaction. The fluorescent spectra of the *cis*-linked polymers **2** show large Stokes shifts compared to those of the cross-conjugated polymer precursors **1**.

Polyoxometalates

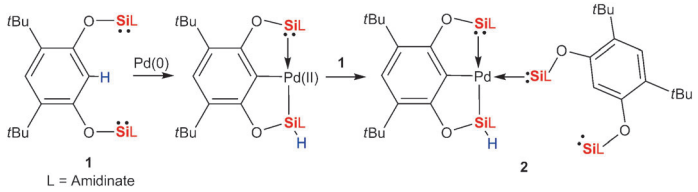
Cyanosilylation of Carbonyl Compounds with Trimethylsilyl Cyanide Catalyzed by an Yttrium-Pillared Silicotungstate Dimer



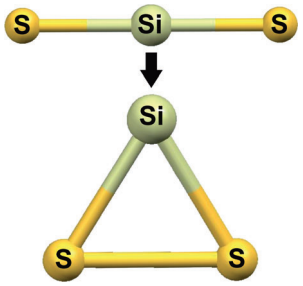
An yttrium-pillared silicotungstate dimer (see picture) catalyzes the cyanosilylation of structurally diverse ketones and aldehydes with trimethylsilyl cyanide (TMSCN). The reactions proceed selectively and afford the corresponding cyanohydrin trimethylsilyl ethers. The catalytic performance is significant, in particular for aldehydes, with a turnover number of 18000 and a turnover frequency of 540000 h^{-1} for *n*-hexanal.

Coordination Chemistry

Synthesis and Unexpected Coordination of a Silicon(II)-Based SiCSi Pincerlike Arene to Palladium

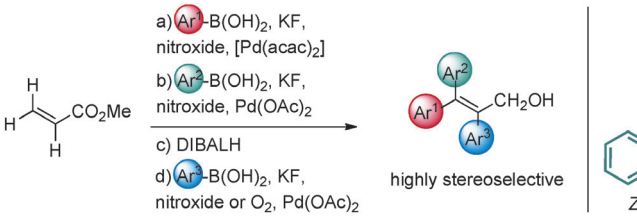


SiCSi to pick up a metal: A bis(silylene) SiCSi pincerlike arene **1** (see scheme) has been synthesized through salt metathesis reaction of the dilithium salt of 2,4-di-*tert*-butyl-resorcinolate with the respective chloro silylene precursor [LSiCl]. Remarkably, **1** reacts with $Pd(PPh_3)_4$ in a molar ratio of 2:1 under loss of all phosphine ligands to give the pincer complex **2**.



A joint effort: By means of high-resolution rotational spectroscopy and highly accurate quantum-chemical calculations, the first observation and characterization of cyclic SiS_2 was achieved. This provides a new perspective on the Walsh rules: Although the cyclic form of SiS_2 is a local and not the global minimum, cyclic isomers of sixteen-electron triatomics containing second or even higher row elements are experimentally accessible.

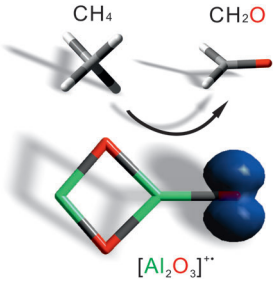
Small-Ring Systems



One, two, and three! Nitroxides and dioxygen serve as oxidants in highly stereoselective oxidative Pd-catalyzed Heck arylations in which aryl boronic acids are used to synthesize triarylalkyl-substituted olefins. The reactions occur under very mild conditions at room temperature. As an example, the threefold sequential arylation of methyl acrylate is the crucial step in the stereoselective synthesis of *Z*-Tamoxifen.

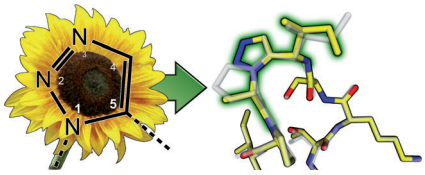
Oxidative Olefin Arylation

Just one step: Reactivity studies demonstrate that in the gas phase $[Al_2O_3]^{\bullet+}$ clusters can efficiently conduct the direct conversion of CH_4 into CH_2O at room temperature (see scheme). The reaction mechanism is highly complex involving oxygen-atom transfer and a double hydrogen-atom transfer.



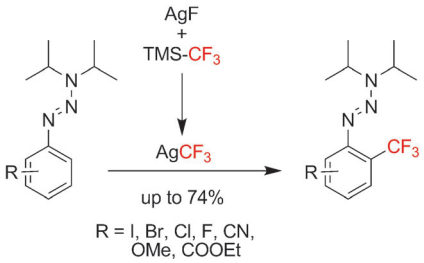
Methane Activation

Flower power: Potent protease inhibitors containing triazolyl mimics of *cis* and *trans* backbone amides were engineered based on the structure of the sunflower trypsin inhibitor 1. The biologically relevant *cis*-Pro motif was successfully replaced with a non-prolyl unit. High-resolution crystal structures of 1,4- and 1,5-disubstituted 1,2,3-triazolyl peptidomimetics can serve in the design of tailor-made Bowman–Birk inhibitors.



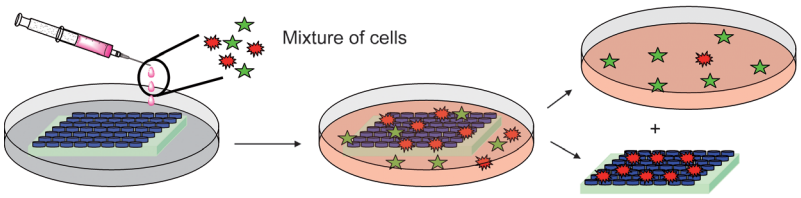
Amide Mimics

Trifluoromethylation



A silver key to add CF_3: In presence of in situ generated $AgCF_3$, it is possible to trifluoromethylate aromatic triazenes in high *ortho* selectivity and good yields by means of a C–H substitution (see scheme). Owing to the further transformation possibilities offered by triazenes, a variety of CF_3-substituted building blocks are then accessible.

Selective Cell Adhesion



Zeolite L nanocrystals can be enantioselectively functionalized and their enantiomorphous SAMs prepared. The adhesion behavior of different cells with these new biomaterials was studied according to the respective surface chirality. This concept was demonstrated for cell separation of primary cells and cell lines (see picture).

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