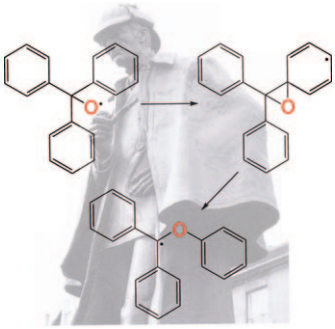
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Author Profile

"My ultimate goal is to assemble/discover artificial (inorganic) biology.
When I was eighteen I wanted to be a fast jet pilot …"
This and more about Leroy (Lee) Cronin can be found on page 6930.

Highlights



Reopening the case: One hundred years after Wieland's original publication, the rearrangement of the trityloxy radical was studied by K. Ingold et al., who investigated the title reaction with the logical reasoning and intellectual prowess of true detectives.

Trityloxy Radical

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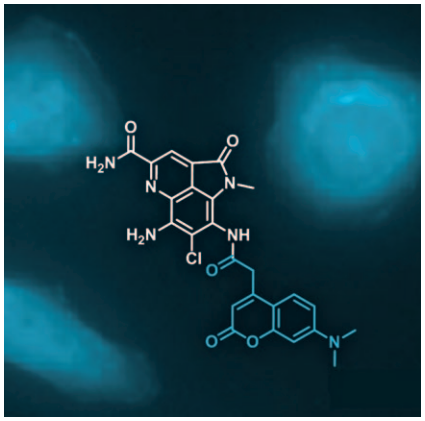
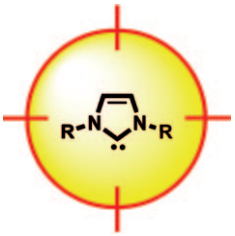


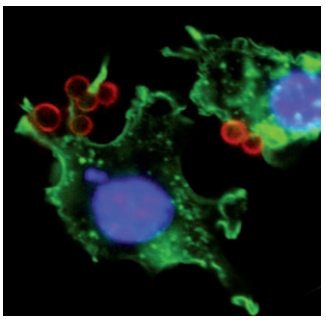
Out of the blue: Ammosamides A (**1**) and B (**2**) were isolated from a marine streptomycete collected at a depth of more than 1600 m. By employing a blue-fluorescent diaminocoumarin conjugate of **2** (see structure), myosin was identified as a cellular target of these antiproliferative natural products. The total synthesis of **1** and **2** has now been completed, thus allowing further elaboration of the chemical biology of these fascinating compounds.

Minireviews

Beyond measure? N-Heterocyclic carbenes (NHCs) have become ubiquitous ligands for organometallic chemistry as well as organocatalysts. The key concepts used for the quantification of the characteristic properties of NHCs are described. The ability to quantify, modify, maximize, or minimize these properties should eventually enable the design, selection, and utilization of tailor-made NHC ligands for a desired catalytic application.



Reviews



Layer-by-layer coating of a sacrificial template followed by dissolution of the template can be used to generate polymeric multilayer capsules. By varying the capsule components and their physicochemical properties, multifunctional microcarriers (red circles) can be designed with high potential for drug delivery.

For the USA and Canada:
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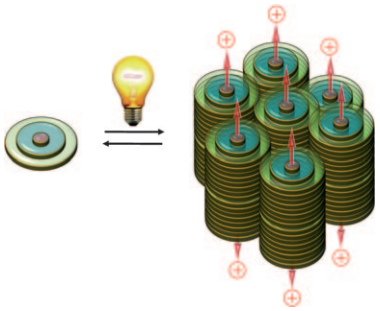
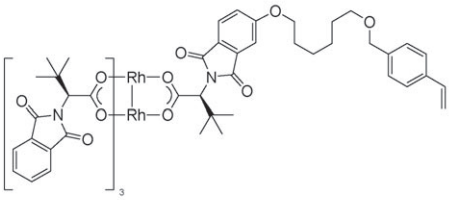
Communications

Let there be more light: Triarylamine-based building blocks respond to visible-light exposure by the formation of cationic radicals that hierarchically self-assemble into molecular wires, which in turn combine within larger fibers (see picture). The stimuli-responsive supramolecular scaffold, which is created by charge transfer and reversibly broken up by heating, prevents the quenching of holes within the wires.



Self-Assembly



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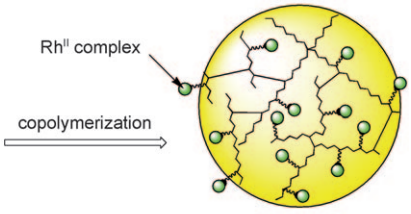
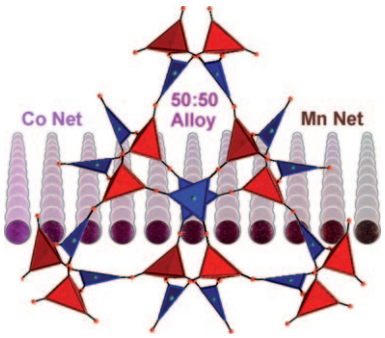


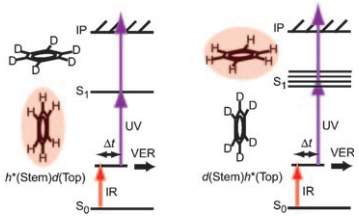
A highly effective immobilization of [Rh_2(*S*-PTTL)$_4$] (PTTL = *N*-phthaloyl-*tert*-leucinate) has been achieved by copolymerization of monomer **1** with styrene and a flexible cross-linker. The immobilized catalyst promoted the title reaction at −78 °C with high enantioselectivity, and could be used for up to 100 cycles with a low level of leaching (0.28 ppm).

Heterogeneous Catalysis



Alloy, alloy: A pure cobalt-based Keggin network linked by W-O-Co interactions is "alloyed" with a pure manganese-based Keggin network, linked by W-O-Mn interactions. These isostructural alloys are solid solutions of the Co and Mn nets. The alloys are prepared by the stoichiometric mixing of the components of each discrete network, leading to a series of single-crystalline mixed transition-metal frameworks with novel redox properties.

Polyoxometalate Frameworks



VERy relaxing: Vibrational energy relaxation (VER) of benzene dimer isotopologues in the CH stretching vibrational level has been investigated by picosecond time-resolved IR–UV pump–probe spectroscopy (see picture, $h = C_6H_6$, $d = C_6D_6$). A remarkable difference is found in the relaxation lifetime: the lifetime of the stem site (110 ps) is 4.5 times shorter than that of the top site (500 ps).

Time-Resolved Spectroscopy

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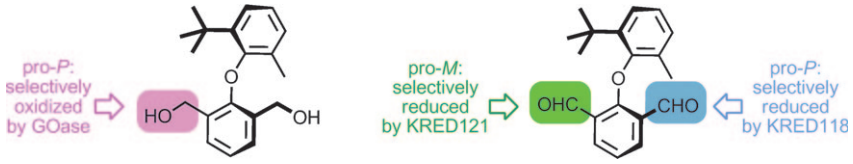
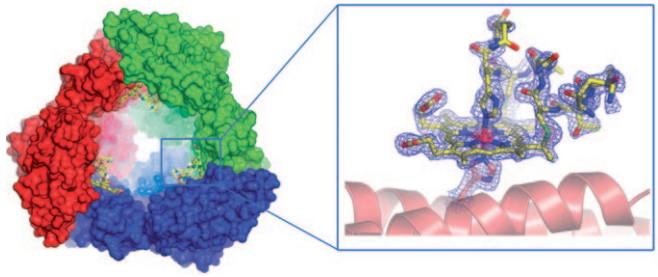


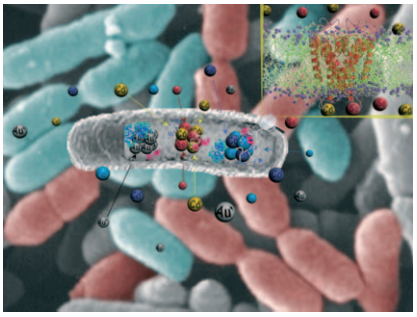
All roads lead to ... atropisomeric diaryl ethers containing a benzylic hydroxy group and an aldehyde unit. The isomers were synthesized in enantiomerically enriched form by desymmetrizing atroposelective enzymatic oxidation (with a galactose oxidase (GOase) variant) or reduction (with a ketoreductase (KRED); see scheme).

Atroposelectivity



Caged to submission: The zinc-ion-directed assembly of tetrahedral protein cages (Zn_{30}:CFMC-1_{12}) in a rhombohedral crystal lattice is presented. The histidine side chains and exposed hydrophobic groups lining up the cavities of these cages enabled a flexible *c*-type heme peptide fragment (a microperoxidase) to be immobilized within and its crystal structure to be determined at 1.9 Å resolution.

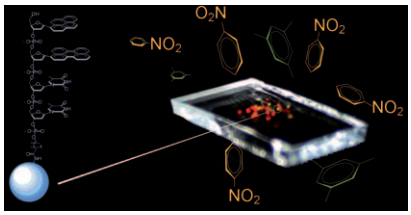
Peptide Structures



A metal-nanoparticle factory: Various metal nanoparticles with tailored optical, electronic, chemical, and magnetic properties were synthesized in vivo in a size-tunable manner in recombinant *E. coli* (see picture) through interaction with the metal-binding protein metallothionein and the metal-binding peptide phytochelatin, which was synthesized by phytochelatin synthase.

Biogenic Nanoparticles

With a response for any occasion: Oligodeoxyfluorosides (ODFs) conjugated to poly(ethylene glycol)–polystyrene beads were used as fluorescent sensors of multiple organic vapors (see picture). The ODFs—DNA-like oligomers in which fluorophores, spacers, and quencher groups replace DNA bases—had sufficient electronic diversity to show a wide range of responses to chemically varied volatile organic compounds.



Fluorescence Sensing

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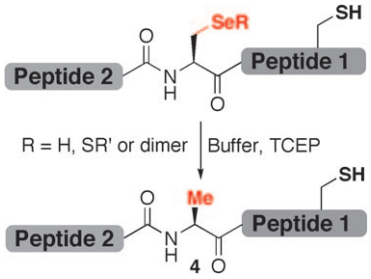
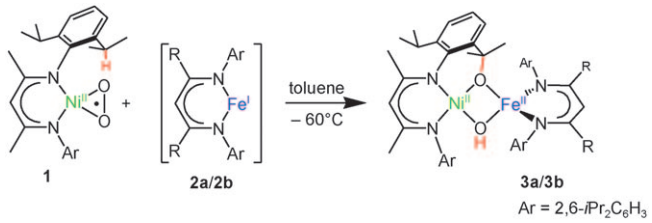


Selective deselenization: Native chemical ligation at selenocysteine is followed by selective deselenization of the selenocysteine to alanine, in the presence of cysteine residues without protecting groups (see scheme). This selectivity is achieved by using the water-soluble tris(2-carboxyethyl)phosphine (TCEP) in the absence of a radical initiator.

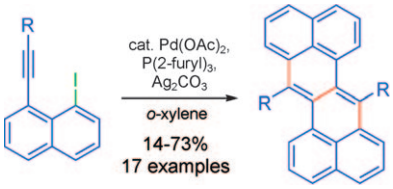
Peptide Ligation



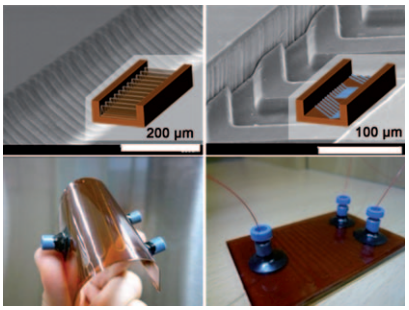
Pool together: Oxidative addition of the superoxo ligand inherent to the nickel(II) superoxide **1** onto iron(I) precursor complexes **2a**/**2b** leads unexpectedly and exclusively to the first NiFe alkoxo hydroxides **3a** (R = Me) and **3b** (R = *t*Bu). The latter result from an unexpected, selective oxygenation of a C–H bond of one of the isopropyl groups at the β-diketiminato ligand coordinated to nickel.

Heterobimetallic Oxygenation

Zethrenes were synthesized by Pd-catalyzed cyclodimerization of 1-ethynyl-8-iodonaphthalenes. The structure of these cycloadducts was confirmed by X-ray crystal analysis. The bond lengths and bond alternation in the crystal structures reveal that the central two six-membered rings of the title compounds lack aromaticity.



Zethrenes



Keeping limber: A monolithic and flexible polyimide film microreactor is introduced for organic reactions and syntheses. Unlike glass microreactors, it is easy to fabricate, yet it is inert to solvents and acids under harsh conditions, unlike other polymer microreactors.

Microreactors

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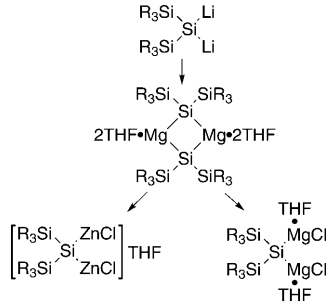
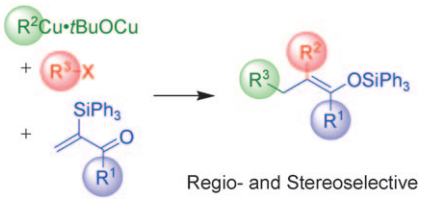


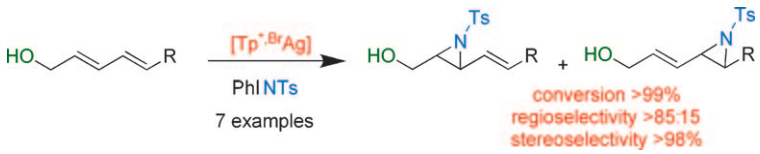
Two metals are better than one: A cyclic 1,1-dimagnesiosilane, a 1,1-di(chloromagnesio)silane, and a 1,1-di(chlorozincio)silane have been synthesized using transmetalation reactions (see scheme; THF = tetrahydrofuran) and characterized by X-ray crystallography. Cyclic 1,1-dimagnesiosilane was studied in redox reactions that led to a lithium-substituted silyl radical and a vicinal 1,2-dilithiosilane.

Silicon Compounds



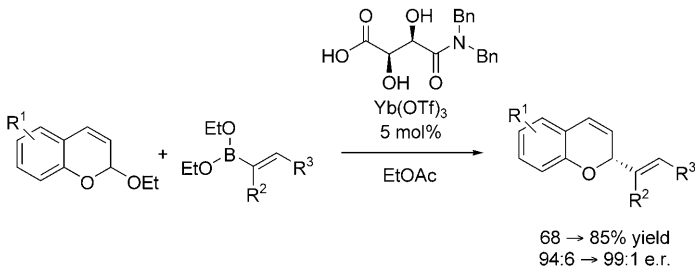
Three components for total control: Trisubstituted silyl enol ethers were prepared by three-component coupling of α-silyl α,β-unsaturated ketones, organocopper reagents, and organic halides with complete regio- and stereoselectivity (see scheme). The reaction proceeded through a 1,3 migration of the silyl group via cyclic silicate intermediates, which controlled the configuration of the silyl enol ethers.

Stereoselective Synthesis



Nitrene transfer: Unsymmetric dienes bearing a terminal hydroxy group can be regio- and stereospecifically converted into vinylaziridines upon nitrene transfer from PhINTs using a silver-based catalyst. Stoichiometric mixtures of dienes and PhINTs were employed at low catalyst loadings (0.5%; see scheme). The method has been applied to the synthesis of (±)-sphingosine and gave good yields in a three-step procedure. Ts = 4-toluenesulfonyl.

Synthetic Methods



Chiral α,β-dihydroxy carboxylic acids catalyze the enantioselective addition of alkenyl and aryl boronates to chromene acetals. The optimal carboxylic acid is the easily available tartaric acid amide shown in the scheme. Spectroscopic and kinetic mechanistic studies demonstrate that an exchange process generates a reactive dioxoborolane intermediate leading to enantioselective addition to the pyrylium ion formed from the chromene acetal.

Asymmetric Catalysis

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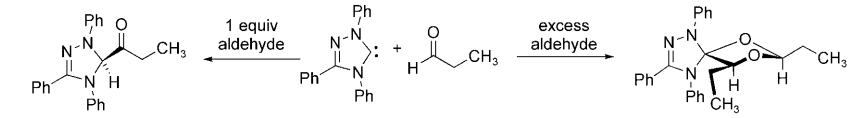
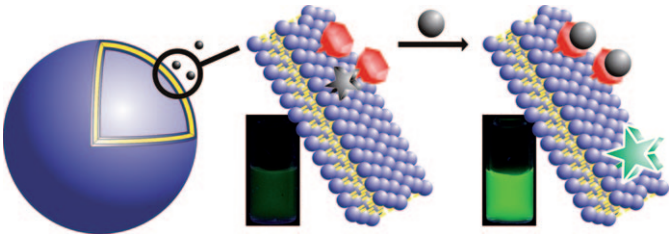


Breslow adduct, keto form **K**: energetic minimum

spirodioxolane **S**: resting state of the catalytic system

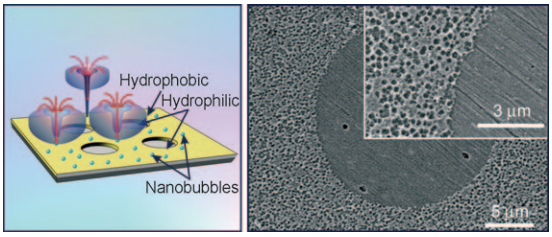
Surprises from a classic: The Breslow intermediate of triazolylidene-catalyzed benzoin condensations was characterized for the first time by NMR spectroscopy in its keto form (**K**, energetic minimum). The hitherto unknown spiro-dioxolane **S**, generated from the carbene catalyst and two equivalents of aldehyde, is the resting state of the catalytic system.

Organocatalysis



Tiny analysts: Co-embedding of amphiphilic binding sites and environment-sensitive dyes in vesicular membranes allows rapid and easy preparation of self-assembled modular chemosensors. The fluorescent particles thus obtained respond to the presence of analytes by changes in their emission intensity.

Luminescence Chemosensors



Sonochemistry at surfaces can be controlled by suitable surface patterning. Bubble nucleation occurs predominantly on hydrophobic surfaces (see picture, left), which thus can be selectively treated by ultrasound. The right-hand picture shows a structurally modified aluminum plate after ultrasound treatment. The inner circular region is hydrophobic, and the outer region is hydrophobic.

Sonochemistry

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

Service

Corrigendum

Bis(1,3-trimethylsilylallyl)beryllium

S. C. Chmely, T. P. Hanusa,*
W. W. Brennessel 5870–5874

Angew. Chem. Int. Ed. **2010**, *49*

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The equation in the artwork for this Communication (DOI: 10.1002/anie.201001866) on page 5870 has been inadvertently rearranged. It should read as follows: