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:*


A. Heller


M. A. El-Sayed


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R. Sarpong


J.-Q. Yu


A. Zakarian

News

Contents

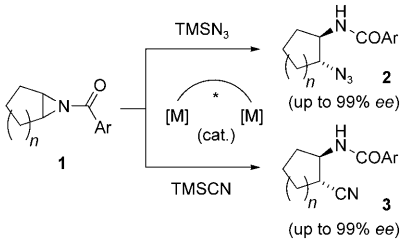
Author Profile

„My favorite piece of research is the recent progress in the generation of purely synthetic protocells. The secret of being a successful scientist is to recognize an innovative idea and to creatively track it."
This and more about Michael Famulok can be found on page 2077.

Books

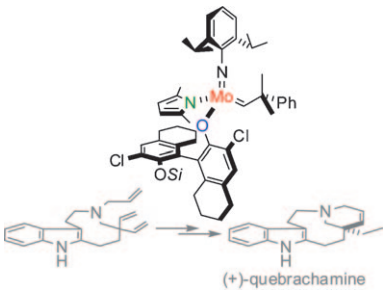
Highlights

Asymmetric Catalysis



Cooperative metal centers in a bimetallic catalyst facilitate the highly enantioselective ring opening of *meso* aziridines **1** with silyl nucleophiles (see scheme; TMS = trimethylsilyl). The 1,2-azidoamides **2** and 1,2-amidonitriles **3** obtained in this way in high yields and with up to 99% *ee* are valuable precursors to enantiomerically pure 1,2-diamines and β-amino acids.

Asymmetric Catalysis



A double flip! The catalyst shown, with a molybdenum stereocenter and monodentate ligands (*Si* = SitBuMe$_2$), promotes asymmetric ring-closing metathesis of a broad range of substrates. Its unprecedented activity originates from its structural fluxionality, which enables double inversion at the metal center in the course of a single catalytic cycle. The catalyst passed the test in a metathesis reaction en route to (+)-quebrachamine (see scheme).

For the USA and Canada:
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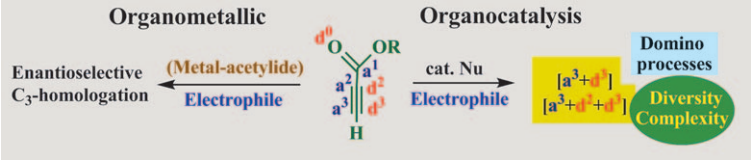
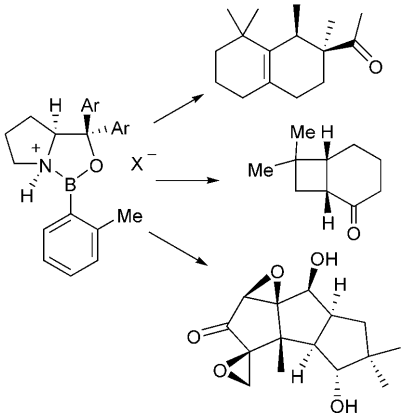
Minireviews



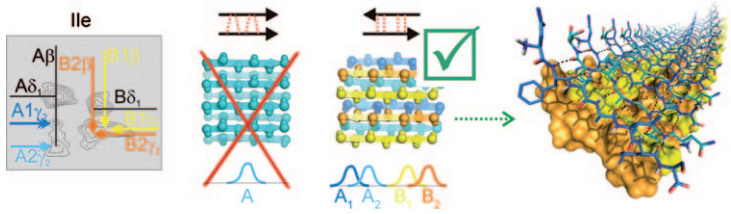
Three that matter: Metal acetylides from alkyl propiolates allow C_3 homologations with transference of their versatile reactivity profile to products that can then react without further elaboration. Metal-free acetylides, which are generated by the action of a good nucleophile on the alkyl propiolate, react with suitable electrophiles through different domino reactions to generate skeletal diversity.

Reviews



Chiral oxazaborolidines can be activated by N-protonation using strong protic acids or by N-coordination with $AlBr_3$ to form very strong chiral Lewis acids. The resulting chiral boron electrophiles (see structure) are powerful chiral catalysts that effectively promote [4+2], [3+2], and [2+2]-cycloaddition reactions with high enantioselectivity.

Communications



The fibril structure formed by the amyloidogenic fragment SNNFGAILSS of the human islet amyloid polypeptide (hIAPP) is determined with 0.52 Å resolution. Symmetry information contained in the easily obtainable resonance assignments from solid-state NMR spectra (see picture), along with long-range constraints, can be applied to uniquely identify the supramolecular organization of fibrils.

Incredibly

iNcOgnitO

...!

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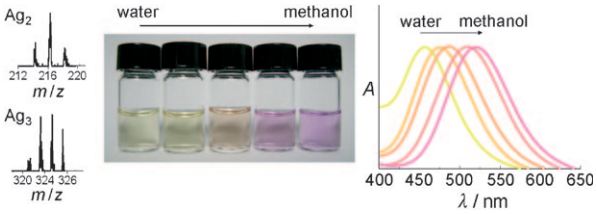
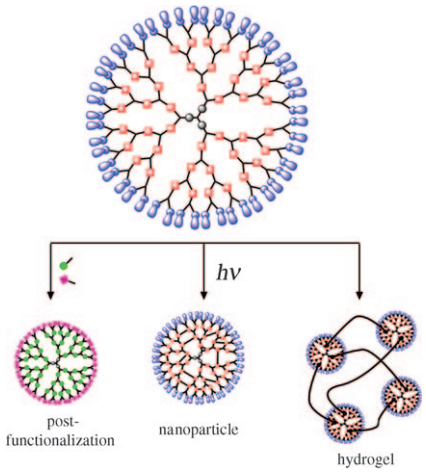


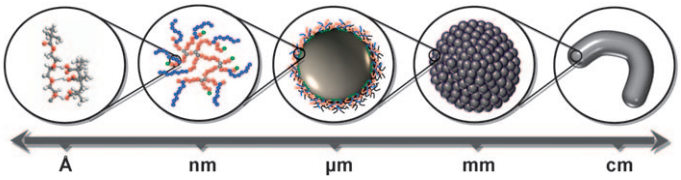
Colorful clusters: Silver nanoclusters consisting of only a few atoms exhibit large chemical-environment-responsive shifts of their optical absorption and emission bands, that is, large solvatochromism (see picture). The photophysical characteristics and electrochemiluminescence of the Ag clusters give them remarkable advantages over larger nanoparticles in applications such as molecular sensing.

Metal Nanoclusters

A fourth wheel: Two sets of bifunctional AB_2C dendrimers having internal acetylene/azides and external hydroxy groups were constructed utilizing benign synthetic protocols. An in situ postfunctionalization strategy was successfully carried out to illustrate the chemoselective nature of these dendrimers. The dendrimers were also transformed into dendritic nanoparticles or utilized as dendritic crosslinkers for the fabrication hydrogels.



Supramolecular Chemistry

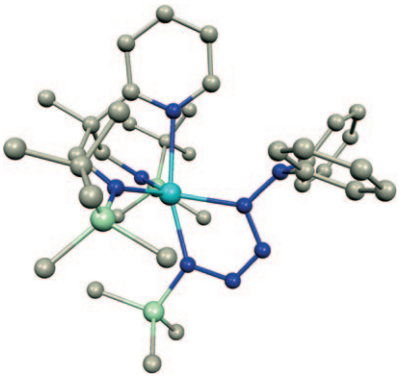


Making and breaking: Stable, functional micrometer-sized emulsion droplets can be assembled into various complex macroscopic liquid structures (see picture). The hierarchical assembly process is mediated by interactions between polymeric surfactant molecules located on the droplet surfaces. These interdroplet interactions are reversible, therefore these "engineered emulsions" can be readily disassembled by using a simple pH switch.

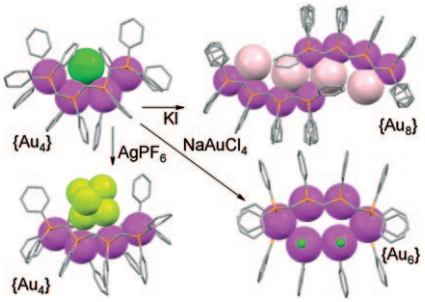
Emulsions

Contents

Breaking the chain: Reaction of a zirconium hydrazinediide with organoazides gives 2-pentazene-1,4-diyl complexes, such as $[Zr(N_2^{TBS}N_{py})\{N(Ad)N_3NPh_2\}]$ (C gray, N blue, Si green, Zr turquoise), by formal [2+3] cycloaddition. Bonding within the N_5 chain is investigated using density functional calculations. These complexes thermally eject N_2 to give side-on bonded diazenides.



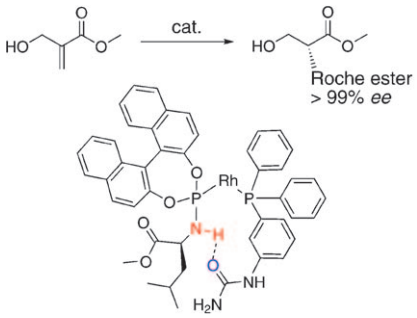
Nitrogen Chains



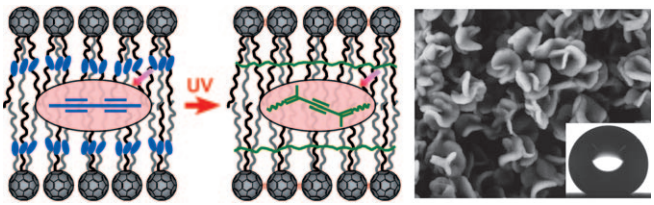
A flexible building block: Flexible tetragold(I) chain complexes supported by a new single methylene-bridged tetraphosphine ligand were synthesized and further transformed into discrete linear octagold(I) $\{Au_8\}$ and cyclic hexagold(I) $\{Au_6\}$ structures by reaction with KI and $NaAuCl_4$, respectively (see picture, Au purple, Cl dark green, PF_6 light green, I pink). The tetragold complexes are also luminescent at room temperature.

Gold(I) Complexes

H bonds make the catalysts! A single hydrogen bond between ligands coordinated to a rhodium center is critical for the formation of pure supramolecular catalysts for asymmetric hydrogenation reactions. The ester group of the amidite ligand (see scheme) also forms a hydrogen bond with the coordinated substrate. Use of the heterocomplex afforded the highest enantioselectivity reported to date for the hydrogenation of several ester substrates.



Asymmetric Catalysis

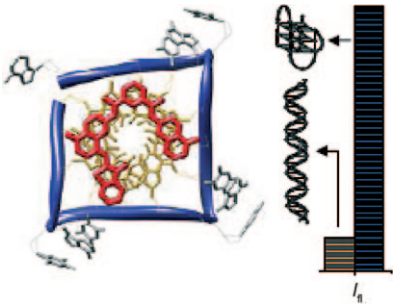


Fullerene flakes: A diacetylene-functionalized fullerene derivative self-organizes into flakelike microparticles (see picture). Both the diacetylene and C_{60} moieties can be effectively cross-linked, which leads to supramolecular materials with remarkable resistivity to solvent, heat, and mechanical stress. Moreover, the surface of the cross-linked flakelike objects is highly durable and water-repellent.

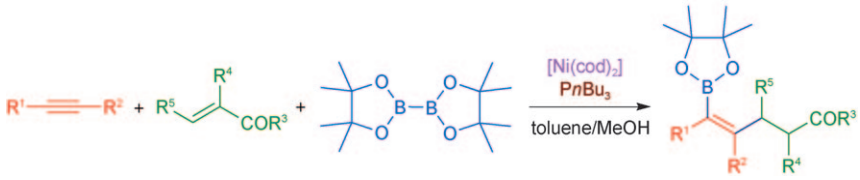
Fullerenes

Contents

Lighting up: A G-quadruplex-specific fluorescent probe was designed combining the specificity of the pyridodicarboxamide motif for guanine quadruplexes and the fluorescence properties of thiazole orange. While the assembly of the two partners through a flexible linker leads to a nonselective probe, merging them in a single, rigid scaffold leads to a dye that elicits the properties required for G-quadruplex sensing.

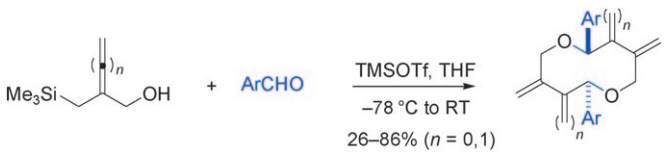


G-Quadruplex DNA



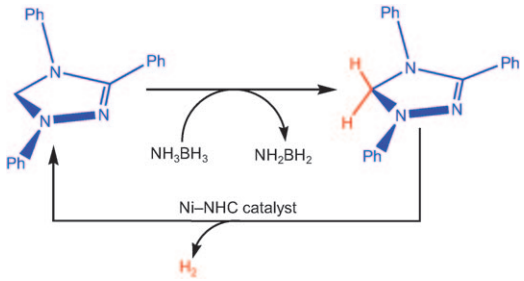
Three-component coupling reactions of an alkyne, an enone, and a diboron reagent provide access to highly substituted alkenyl boronates in good to excellent yields (see scheme). The coupling is highly regio- and stereoselective, and the products are amenable to further functional-group transformations. R^1,R^2 = H, alkyl, aryl, CO_2Me; R^3 = alkyl, Ph; R^4,R^5 = H, alkyl.

Multicomponent Reactions



Double or nothing: The title reaction converts a range of aromatic aldehydes and allenylmethyl/allyl silanes into 1,6-dioxecane derivatives in good to excellent yields (see scheme; Ar = aryl, Tf = triflate, THF = tetrahydrofuran, TMS = trimethylsilyl). In addition, the bisdiene product has been transformed into the corresponding tricyclic compound through a Diels–Alder reaction.

Synthetic Methods

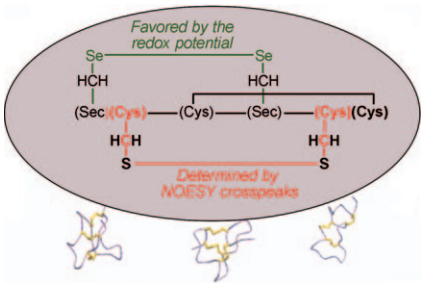


Enders' N-heterocyclic carbene (NHC) dehydrogenates ammonia–borane with a relatively low barrier, producing NH_2BH_2 and NHC–$(H)_2$. The nickel NHC catalyst present in the reaction media can activate the NHC–$(H)_2$ produced to regenerate the free NHC and release H_2. The release of free NHC enables further dehydrogenation of ammonia–borane.

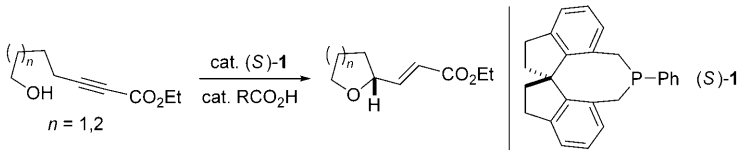
Hydrogen Storage

Contents

Building bridges: The use of diselenide and selectively ($^{15}N/^{13}C$)-labeled disulfide bridges is combined to give improvements in oxidative folding and disulfide mapping. Conotoxin analogues, each with a pair of selenocysteines (Sec) and labeled cysteines (see scheme, red), exhibited significantly improved folding and the labeled cysteines allow correctly folded species to be rapidly identified by NMR spectroscopy.

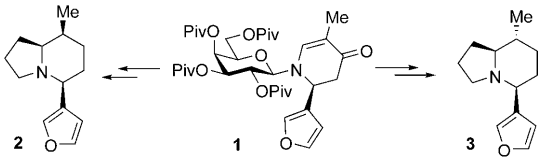


Integrated Oxidative Folding



Chiral phosphepine 1 catalyzes the transformation of an array of hydroxy-2-alkynoates into saturated oxygen heterocycles with good enantioselectivity. Phenols are also shown to participate in such phosphine-catalyzed cyclizations, including an asymmetric variant. This method provides a new approach to the enantioselective synthesis of tetrahydrofurans, tetrahydropyrans, and dihydrobenzopyrans.

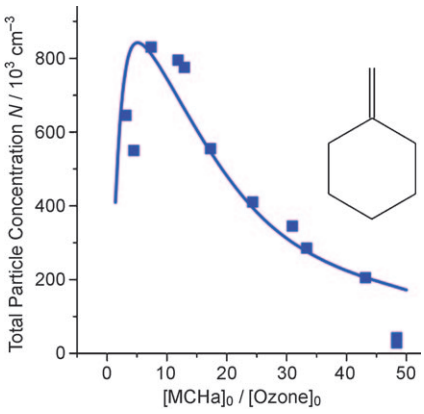
Asymmetric Catalysis



An animalic note: The first total synthesis of the all-*cis* nupharamine **2**, an alkaloid from beaver castoreum, is based on the stereoselective domino Mannich–Michael reaction of *N*-galactosylfurylaldimine to give **1** (Piv = pivaloyl), subsequent conjugate cuprate addition, and stereoselective protonation of the enolate. These reactions are all controlled by the carbohydrate. Protonation of the enolate after cleavage of the auxiliary leads to epimer **3**.

Natural Product Synthesis

The new approach of kinetically controlled ozone removal suppresses particle formation in laboratory ozonolysis experiments for methylcyclohexene and methylenecyclohexane (MCHa) at excess alkene concentrations (see graph). The results support the hypothesis that peroxy radicals are involved in organic nucleation and particle-growth mechanisms.



Aerosol Chemistry

Contents

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

Pentagerma[1.1.1]propellane: A Combined Experimental and Quantum Chemical Study on the Nature of the Interactions between the Bridgehead Atoms

D. Nied, W. Klopper*
F. Breher* ——— **1411–1416**

Angew. Chem. Int. Ed. **2009**, *48*

DOI 10.1002/anie.200805289

In this Communication reference [18d] contains an error. The correct reference is shown here.

[18] a) L. R. Sita, I. Kinoshita, *J. Am. Chem. Soc.* **1992**, *114*, 7024; b) L. R. Sita, I. Kinoshita, *J. Am. Chem. Soc.* **1991**, *113*, 5070; c) L. R. Sita, I. Kinoshita, *J. Am. Chem. Soc.* **1990**, *112*, 8839; d) L. R. Sita, R. D. Bickerstaff, *J. Am. Chem. Soc.* **1989**, *111*, 6454.