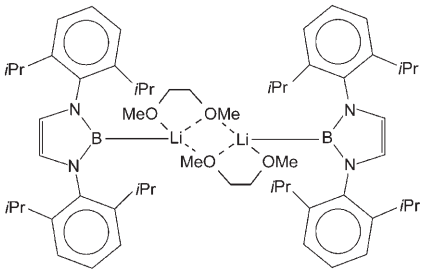
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

News

Books

Highlights

B negative: By reduction of a 2-bromo-1,3,2-diazaborole Yamashita, Nozaki, and co-workers have obtained the first three-coordinate boryl anion (see formula), which provides an unprecedented and synthetically highly useful source for a nucleophilic boron species.



Boryl Anions

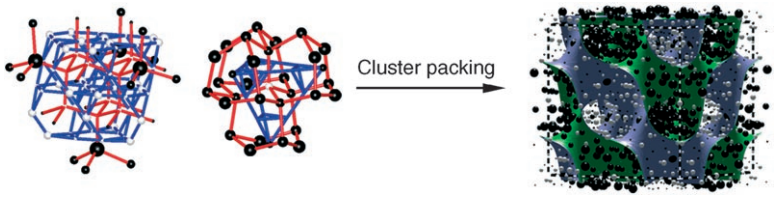
Minireviews

Calcium supplements for Grignard: The easy access of aryl calcium compounds in high yields now offers the possibility of investigating the properties and chemical behavior of these heavy Grignard reagents (see picture; C black, Ca purple, Cu yellow, O red). The key points are the nature of activation of the metal prior to use and the use of low reaction and handling temperatures to prevent side and decomposition reactions.

Heavy Grignard Reagents

Contents

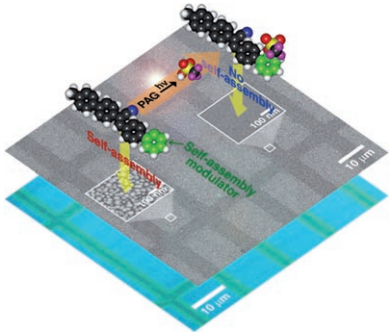
Reviews

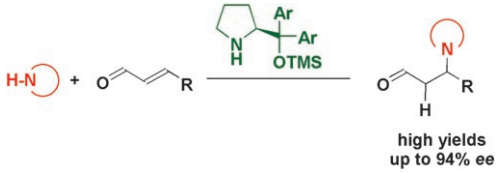


Inorganic, and yet more complex than an enzyme? The giant unit cells of Mg_2Al_3, $NaCd_2$, and Cu_4Cd_3 have challenged geometers of nature—so many beautiful polyhedra and networks to choose from. Could quantum mechanics help pick among alternative patterns? Indeed, simple calculations highlight building blocks derived from the $MgCu_2$ structure type, which pack together in interpenetrating regions of polar and nonpolar bonding (see scheme for $NaCd_2$).

Communications

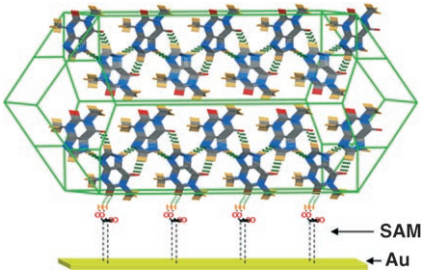
Bottom-up and top-down nanofabrication: A fluorescent organic molecule bearing a self-assembly modulator was assembled in situ through a vapor-driven self-assembly process into strongly fluorescent spherical nanoparticles (about 30 nm in diameter) in the photochemically delineated regions of a polymer matrix (see picture; PAG: photoacid generator).





Must love cats.! Chiral amines catalyze the enantioselective addition of N-heterocyclic compounds to α,β-unsaturated compounds in high yields and with enantioselectivities of up to 94% *ee* (see scheme; TMS = trimethylsilyl). The intermediates and transition states for the catalytic cycle were identified by performing DFT calculations.

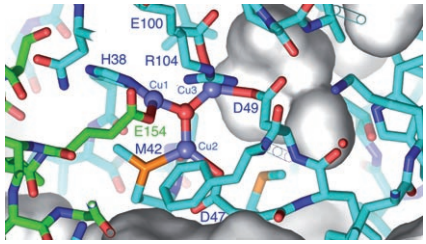
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 5685/5168 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



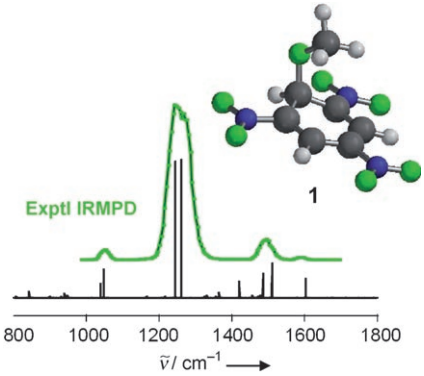
SAMs in charge: The monohydrate and anhydrous forms of theophylline crystallize concomitantly from ethanol solutions, but hydrophilic thiol self-assembled monolayers (SAMs) promote the selective growth of the anhydrous form (see picture; C gray, H yellow, N blue, O red). This selectivity is a result of interfacial hydrogen bonding and geometric epitaxy.

Drug Crystal Growth

A pocketful of coppers: Redox potentiometry and EPR experiments have confirmed that the active site of the particulate methane monooxygenase (pMMO), a membrane-bound enzyme that hydroxylates methane to methanol under ambient conditions, consists of one trinuclear copper cluster (see picture) and one type 2 copper site, in addition to the dinuclear copper cluster revealed previously by X-ray crystallography.

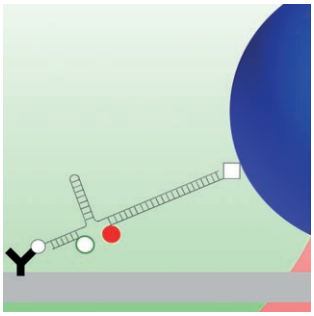


Bioinorganic Chemistry



Proof positive: Infrared multiphoton dissociation (IRMPD) spectroscopy, with the tunable IR radiation of a free-electron laser source, provides positive identification of alkoxide adducts of 1,3,5-trinitrobenzene as prototypical anionic σ complexes in the gas phase (see calculated IR spectrum of **1** under the experimental IRMPD spectrum; N blue, O green, C gray, H light gray).

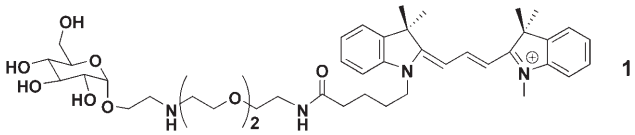
Gas-Phase Spectroscopy



Don't FRET: The first successful combination of optical-tweezers force microscopy and single-molecule fluorescence resonant energy transfer (FRET) is demonstrated with a force sensor based on a DNA hairpin (see picture). As the hairpin is opened and closed by the optical tweezers, the structural change is simultaneously monitored by the FRET emission from fluorescence labels.

Single-Molecule Manipulation

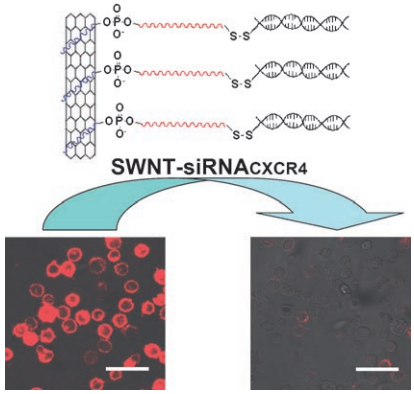
Contents



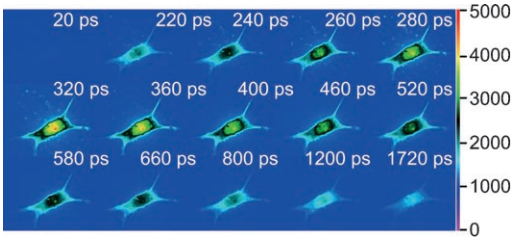
Tracing glucose uptake: Fluorescent glucose analogues were synthesized, and the importance of stereochemistry for cellular uptake efficiency was demonstrated. The chiral bioprobe **1** showed superior properties as a glucose-uptake tracer. The cellular uptake of **1** was demonstrated under various concentrations of D-glucose. A screening system was developed for the discovery of anticancer agents by the measurement of glucose uptake in cancer cells with **1**.

Fluorescent Bioprobes

Special delivery: Functionalized single-walled nanotubes (SWNT) can be used as molecular transporters to shuttle short interfering RNA (siRNA) into human T cells and primary cells and silence the expression of HIV-specific cell-surface receptors and coreceptors (see picture; scale bars 40 μm). This silencing effect, known to block HIV viral entry and reduce infection, is superior to that observed with conventional liposome-based nonviral delivery agents.

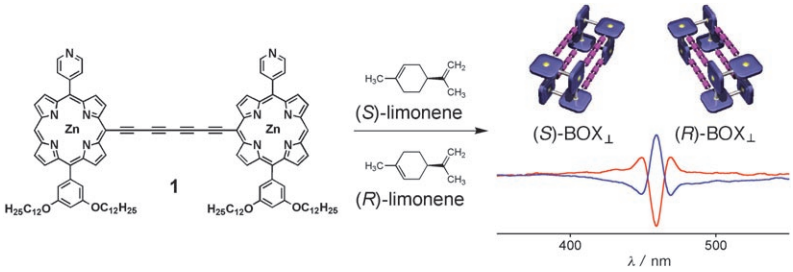


Nanobiotechnology



Every nucleolus has a silver lining: Formation of silver nanoclusters by fluorescence photoactivation was used for the staining of cells at low silver nitrate concentrations and ambient temperature. The picture shows picosecond lifetime images of peptide-encapsulated silver nanoclusters within NIH 3T3 cells.

Cell Staining

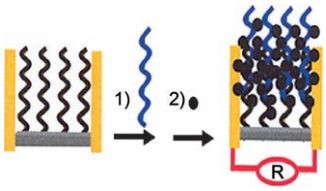


The surrounding shapes the box: The zinc porphyrin dimer **1** bearing pyridyl groups can chiroptically sense an asymmetric hydrocarbon, such as limonene, by forming the homochiral box-shaped tetrameric assembly $BOX_{\perp}$. As the $BOX_{\perp}$ formed is enantiomerically enriched, the optical purity as well as the absolute configuration of the solvent limonene can be determined.

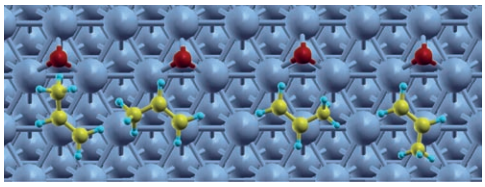
Molecular Recognition

Contents

Build a bridge: Strong interactions between zirconium-activated indium tin oxide (ITO) nanoparticles and phosphates are utilized to label nucleic acids with multiple ITO nanoparticles under very mild conditions. The electrically conductive ITO nanoparticle network formed bridges the gap between a pair of interdigitated electrodes, allowing the detection of nucleic acids at subpicomolar levels with high specificity.



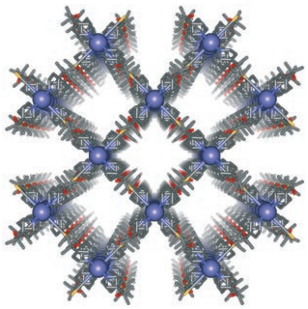
Biosensors



Gotta have copper: DFT studies indicate that the performance of heterogeneous epoxidation catalysts depends on the first step in the reaction between oxygen atoms and propylene molecules coadsorbed on the metal surface (see picture; C yellow, H light blue, O red). The high basicity of oxygen atoms on silver favors allylic hydrogen stripping, whereas the low basicity of oxygen atoms on copper favors metallacycle formation and subsequent epoxidation.

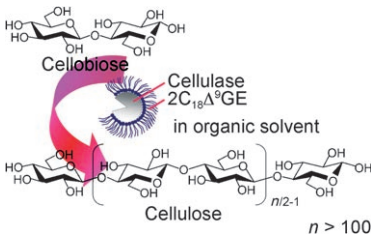
Heterogeneous Catalysis

Influential guests: An abrupt spin-crossover transition is exhibited by a nanoporous framework material that consists of interpenetrated two-dimensional grids linked by hydrogen-bonding interactions. Desorption of guest molecules from the highly robust host lattice occurs by a single-crystal-to-single-crystal transformation and leads to subtle changes in the framework structure and spin-crossover properties.



Spin Crossover

High and dry: The synthesis in vitro of longer-chain cellulose with more than 100 anhydrous glucopyranose units in the polymer has been performed by a new technique for glycosynthesis. This method uses enzymatic polymerization with enzyme/surfactant complexes that act in nonaqueous organic media.



Nonaqueous Biocatalysis

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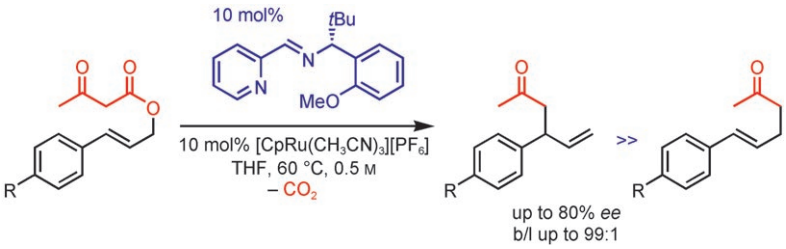
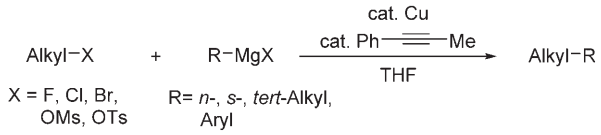


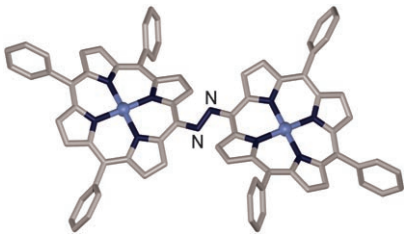
Synthetic Methods

Simple ligands, catalyst, and conditions: The combination of readily prepared unsymmetrical pyridine–imine ligands and $[CpRu(CH_3CN)_3][PF_6]$ ($Cp = C_5H_5$) affords regio- and enantioselective Carroll rearrangements (see scheme; b/l = branched-to-linear ratio). This reaction represents the first example of Ru-catalyzed enantioselective C–C bond-forming allylic substitution.



Cross-Coupling Reactions

A general get-together: The Cu-catalyzed cross-coupling reaction of primary-alkyl halides with primary-, secondary-, and tertiary-alkyl and phenyl Grignard reagents proceeds efficiently in THF under reflux in the presence of 1-phenylpropyne (see scheme). The reaction is also applicable to alkyl mesylates (OMs) and tosylates (OTs). The reactivities of alkyl–X with a Grignard reagent increase in the order X = Cl < F < OMs < OTs < Br.



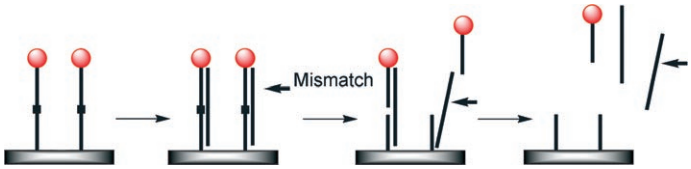
Porphyrinoids

Excellent conjugation: The novel azoporphyrins (1,2-bis(porphyrinyl)diazenes) have been prepared by using copper-catalyzed coupling of primary amines. The structure of the azo(triphenylporphyrin) was determined by X-ray crystallography (see picture). The azo linker provides an excellent conjugating pathway for expansion of porphyrin π conjugation.

The elusive triplet state of indigo (see picture) has been fully characterized by energy-transfer pulse radiolysis and photoacoustic calorimetry. The triplet energy is (1.04 ± 0.10) eV and the singlet-to-triplet intersystem crossing yield in solution is $\phi_{ISC} = 0.0066$. Inefficient intersystem crossing, low triplet energy, and fast internal conversion of the singlet state likely contribute to the high stability of indigo.

Triplet Indigo

Contents



Game, set, and mismatch: In a new method for the detection of base-pair mismatches, an immobilized DNA strand with a cleavage site (black square) and a detection tag (red circle) is hybridized with the target strand. If the target nucleotide has a mismatch, then the marker is released from the solid phase (see scheme).

Analytical Methods

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigendum

The authors wish to cite an additional paper. In 2002, Doris and co-workers reported the reduction of α,β-unsaturated ketones in the presence of [Cp_2TiCl] and MeOH via free-radical chemistry. This observation is closely related to that reported by the authors the same year on the reduction of carbon radicals in the presence of [Cp_2TiCl] and water but was not cited in the present article. The authors apologize for the oversight. Reference [4] should therefore read as follows:

[4] a) A. F. Barrero, J. E. Oltra, J. M. Cuerva, A. Rosales, *J. Org. Chem.* **2002**, *67*, 2566–2571; b) for related observations on the reduction of α,β-unsaturated ketones in the presence of [Cp_2TiCl] and MeOH, see: L. Moisan, C. Hardouin, B. Rousseau, E. Doris, *Tetrahedron Lett.* **2002**, *43*, 2013–2015.

Water: The Ideal Hydrogen-Atom Source in Free-Radical Chemistry Mediated by Ti^{III} and Other Single-Electron-Transfer Metals?

J. M. Cuerva,* A. G. Campaña, J. Justicia, A. Rosales, J. L. Oller-López, R. Robles, D. J. Cárdenas,* E. Buñuel, J. E. Oltra* ——— **5522–5526**

Angew. Chem. Int. Ed. **2006**, *45*

DOI 10.1002/anie.200600831

