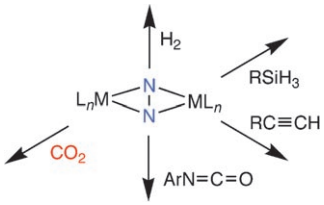
VIP ***The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:***

Obituary

Books

Highlights

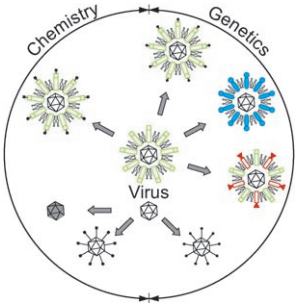
Side-on matters: When dinitrogen bridges two Group 4 metal centers in the side-on binding mode, the reactivity of the N_2 unit is enhanced, as evidenced by unprecedented reactions with H_2, alkynes, silanes, isocyanates, and now carbon dioxide (see scheme). This Highlight summarizes a number of recent breakthroughs in dinitrogen functionalization by bimetallic Group 4 complexes, culminating with the reaction of CO_2 with a dihafium dinitrogen derivative.



Dinitrogen Functionalization

Minireviews

Useful agents: Viruses as nanoparticles of biological origin offer great opportunities for the design of novel materials. Precise control of their surface chemistry, together with the possibility of genetically engineering the inbuilt genome, turns viruses into a unique tool for the fabrication of multifunctional materials and devices.

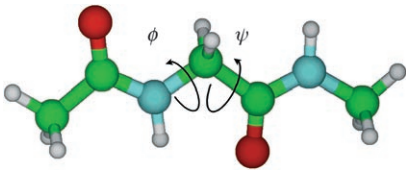


Nanomaterials

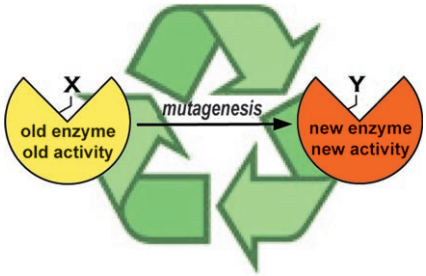
Contents

Reviews

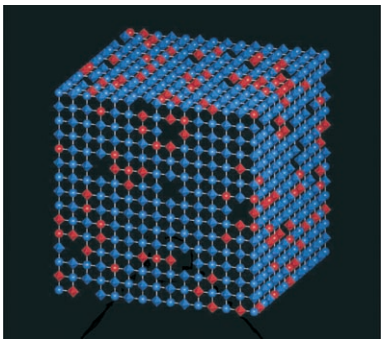
Far-reaching consequences: Charge transfer in peptides and proteins often leads to reactivity at a distal point. This process involves very fast facile molecular motions on a time scale of 100 fs, which is unique to peptides. The principal motions are found to be the dihedral motions between neighboring amino acids around the Ramachandran angles (ψ and ϕ in the model peptide; green C, gray H, blue N, red O).



Reduce, reuse, recycle: Enzymes catalyze a wide variety of chemical reactions. However, suitable enzymatic catalysts are lacking for many useful transformations. New catalytic activities arise from mutations in the active site, suggesting that the pool of existing enzymes can be a promising starting point for the creation of catalysts for nonbiological reactions. Often, a single point mutation is sufficient to endow an enzyme with a new function.

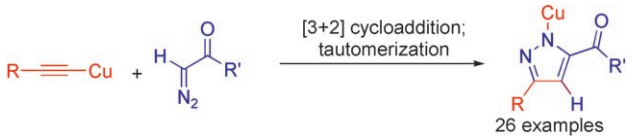


Communications



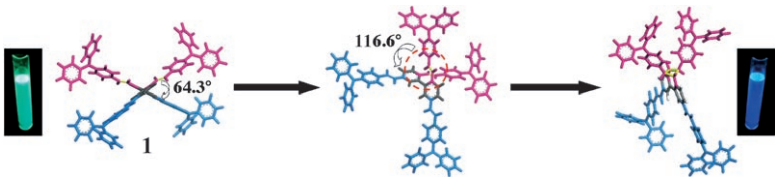
Multiferroic material: $Rb^{I}_{0.82}Mn^{II}_{0.20}Mn^{III}_{0.80}[Fe^{II}(CN)_6]_{0.80}[Fe^{III}(CN)_6]_{0.14}\cdot H_2O$ (see picture; Mn^{II} red octahedra, Fe^{III} red spheres, Mn^{III} blue octahedra, Fe^{II} blue spheres, CN white lines, gaps are Fe vacancies; H_2O omitted) displays both ferroelectricity, explained by a mixing of Fe^{II}, Fe^{III}, Fe vacancies, Mn^{II}, and Jahn–Teller-distorted Mn^{III} centers, and ferromagnetism, caused by a parallel ordering of the magnetic spins of Mn^{III}.

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.



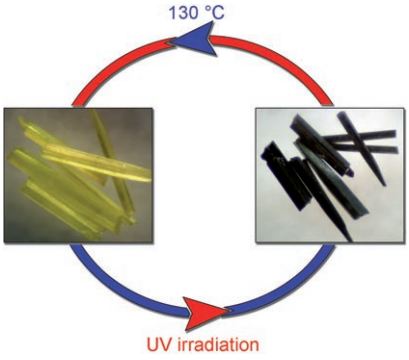
HOMO-logous: The copper-mediated cycloaddition of alkynes with diazo carbonyl compounds to give pyrazoles is reminiscent of the copper-catalyzed cycloaddition of alkynes and azides. The formation of the copper acetylide is proposed to narrow the energy gap between the highest occupied molecular orbital (HOMO) of the alkyne and the lowest unoccupied molecular orbital (LUMO) of the diazo compound.

Dipolar Cycloaddition Reactions



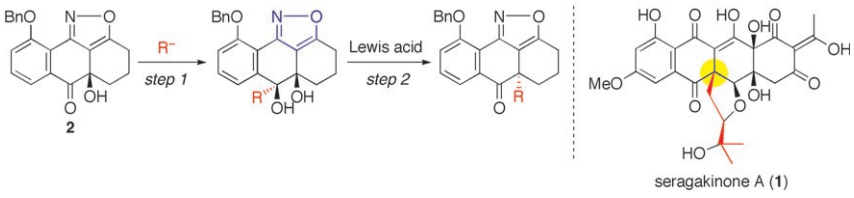
Extremely mild conditions are required for an intramolecular thermal [2+2] cycloaddition in the swivel-cruciform molecule **1**. As a result of the relatively free rotation about the biphenyl bond in **1** (see picture, left) a conformation is accessible in which the alkene bonds of the two *ortho* substituents are brought into proximity in the required orthogonal arrangement, and the intramolecular cycloadduct (right) is formed at room temperature.

Intramolecular Cycloaddition



Color scheme: Reversibly photochromic crystals of (MV)Bi_2Cl_8 (methyl viologen, MV^{2+}: *N*,*N*′-dimethyl-4,4′-bipyridinium) show structural variations before and after UV irradiation. Color reversion is accomplished by heating in air (see picture). $([Bi_2Cl_8]^{2-})_\infty$ double-octahedral chains serve as electron donors to in situ generated MV^{2+} dications.

Photochromic Crystals



Underappreciated and neglected, isoxazoles are extremely good at stabilizing α cations. This ability is exploited in a method for the stereocontrolled introduction of angular substituents as found in polyketide-derived polycyclic natural products, such as **1**. In a two-step process, the stereoselective addition of a nucleophile to the ketol **2** is followed by a regio- and stereospecific pinacol rearrangement. Bn = benzyl; R = allyl, aryl, heteroaryl, vinyl.

Asymmetric Synthesis

For a Professional Touch

NALIZED • POPULAR • FAST • PERSONALIZED • POPULA

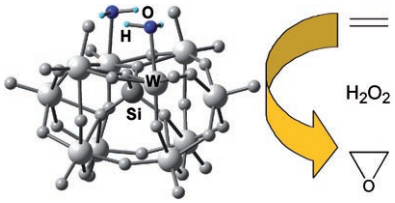
- Reprints of your Article
- High-Resolution PDF
- Personalized Reprints – for example, a bound volume of all your Wiley-VCH articles
  – with your company logo and your advertisement

REPRINTS - YOUR TICKET TO SUCCESS! - TO ORDER AT ANY TIME!

WILEY-VCH

www.wiley-vch.de

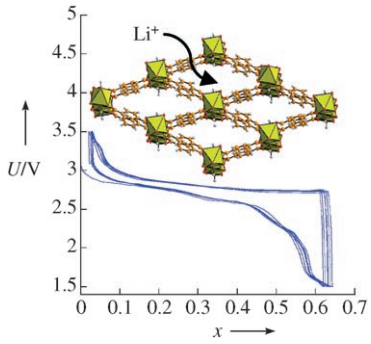
Please contact: Carmen Leitner
Chem-reprints@wiley-vch.de



Water in the lagoon: A fast catalytic epoxidation of both terminal and internal double bonds was promoted by the regioselective tetraprotonation of the polyoxometalate γ-$[(SiO_4)W_{10}O_{32}]^{8-}$ (see picture), which leads to the localization of two water molecules on the reactive lacunary site. This mechanism was supported by evidence from kinetic, spectroscopic, and computational studies.

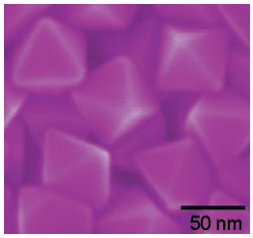
Polyoxometalates

There's more to LiFe: When used as an electrode in a lithium half cell, the metal–organic framework $[Li_xFe^{II}{}_xFe^{III}{}_{1-x}(OH)_{0.8}F_{0.2}L]$ ($L = O_2CC_6H_4CO_2$) shows a reversible redox process around 3.0 V versus Li^+/Li^0 with interesting capacity retention and rate capability (see voltage profile for a $[Li_xFe(OH)_{0.8}F_{0.2}L]$ half cell; inset: representation of lithium insertion upon oxidation to Li^+).

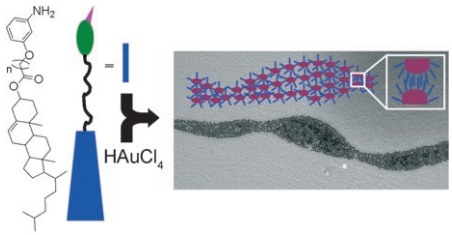


Microporous Materials

Pieces of eight: Single-crystalline Au nano-octahedra with well-defined shape and tunable size can be synthesized by a modified polyol process. The octahedral Au nanocrystals have sharp corners and display optical properties that are sensitive to the crystal sizes and the truncation of the tips.



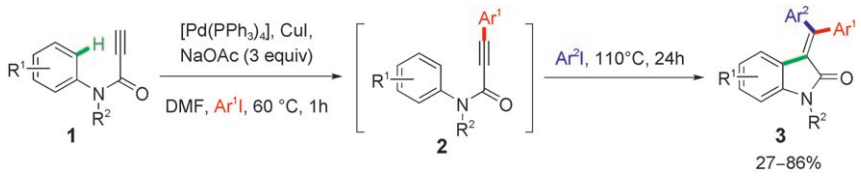
Nanocrystals



Going through a phase: By using simple glass-forming liquid crystals (LCs) in situ, gold nanoparticles (GNPs) were synthesized shape selectively and assembled spontaneously to generate ribbonlike patterns that are replicas of native LC organizations. This remarkable approach afforded boomerang- and V-shaped GNPs.

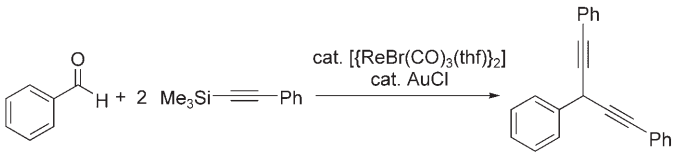
Liquid Crystals

Contents



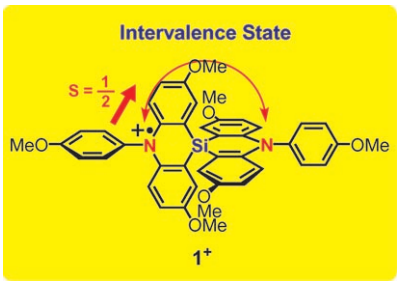
3-3-1 Formation: $[Pd(PPh_3)_4]$/CuI serves as an efficient catalyst for the reaction of three readily available starting materials to give 3-(diarylmethylene)indolin-2-ones **3** through a sequence of intermolecular Sonagashira reaction/intermolecular carbopalladation/C–H activation/C–C bond formation (see scheme). Three C–C bonds are thereby formed as a result of three distinct catalytic cycles with one catalyst. DMF = *N*,*N*-dimethylformamide.

Domino Reactions



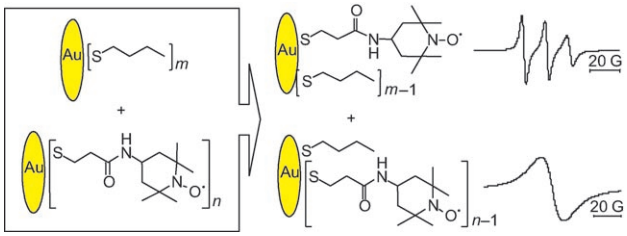
Very couply! Coupling reactions of propargyl or benzyl alcohols with allyl- or alkynylsilanes proceed efficiently using $[\{ReBr(CO)_3(thf)\}_2]$ as catalyst. Additionally, diethynylmethane derivatives were obtained by the reaction of aromatic aldehydes with trimethyl(phenylethynyl)-silane in the presence of both the rhenium complex and AuCl (see scheme).

Cross-Coupling



Intriguing electronic properties were observed for the radical cation $\mathbf{1}^+$ of a spiro-fused bis(triarylamine). In a new example of intramolecular spin transfer (IST) in organic intervalence systems connected by a non-π-conjugated bridging unit, the as-prepared radical cation $\mathbf{1}^+$ exhibited thermally activated IST. Furthermore, it was found that $\mathbf{1}^+$ decomposes slowly to the tri-*p*-anisylamine radical cation.

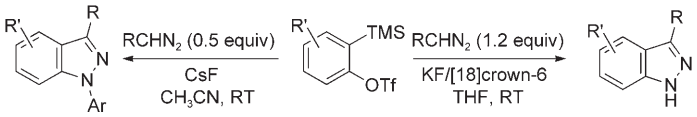
Molecular Electronics



Jump up and down: EPR spectroscopy was used to monitor hopping of spin-labeled ligands between Au nanoparticles. The slow interparticle exchange affects approximately 20% of the binding sites on the nanoparticle surface. The kinetic analysis showed that this reaction follows a dissociative mechanism with ligand desorption in the rate-determining step. EPR = electron paramagnetic resonance.

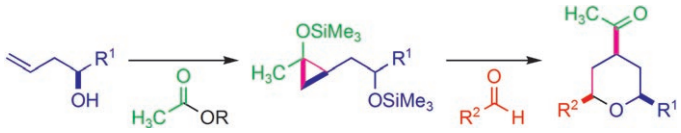
Ligand Exchange

Contents



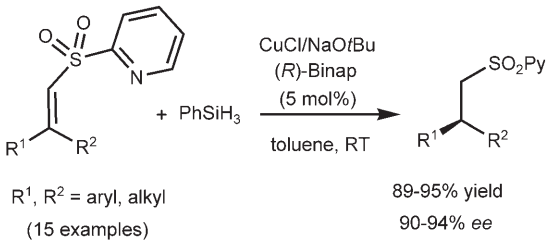
Take your pick: Both N-unsubstituted and 1-aryl 1*H*-indazoles are available in good to high yields through the [3+2] cycloaddition of benzynes derived from *o*-silylaryl triflates with diazomethane derivatives (see scheme). In the presence of KF/[18]crown-6, the N-unsubstituted 1*H*-indazole is formed, whereas the 1-arylated product is obtained regioselectively with CsF and an excess of the triflate.

Synthesis of Heterocycles



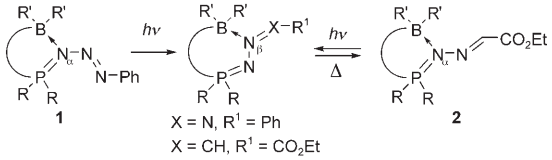
A convenient method for preparing all-*cis* 2,4,6-trisubstituted tetrahydropyrans and the corresponding 2,6-*trans* isomers has been developed. This trimethylsilyl triflate mediated coupling of cyclopropanols with a 2-hydroxyalkyl side chain to aldehydes (see scheme) is also suitable for the coupling of two large subunits to generate structural complexity in a rapid and highly convergent manner.

Cyclic Ethers



Access to a chiral sulfone: Asymmetric conjugate reduction of β,β-disubstituted α,β-unsaturated 2-pyridylsulfones with silanes under Cu^{I}/binap catalysis provides chiral sulfones with excellent chemical yields and enantioselectivities (see scheme). These enantioenriched 2-pyridylsulfones are versatile intermediates in the preparation of a wide variety of functionalized chiral compounds. binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl.

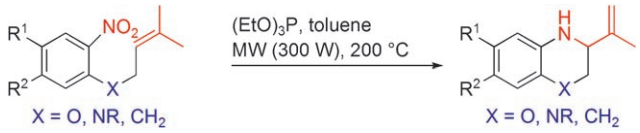
Asymmetric Catalysis



Stable relations: Reaction of phenylazide with a phosphine borane derivative gives rise to an intramolecularly stabilized phosphazide **1** (R = *i*Pr, R′ = mesityl) that undergoes an unprecedented photoisomerization process associated with a change from an $N_{\alpha}\rightarrow B$ to an $N_{\beta}\rightarrow B$ interaction (see scheme). The generality and possible reversibility of such phenomena are demonstrated with the related phosphazine adduct **2**.

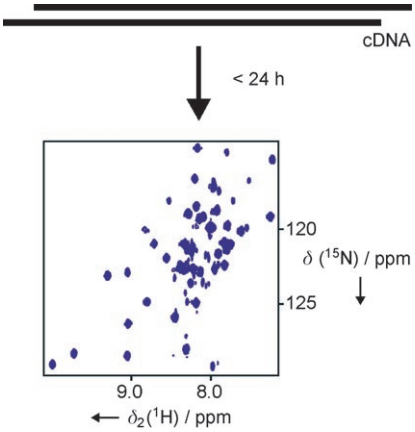
Phosphorus Heterocycles

Contents



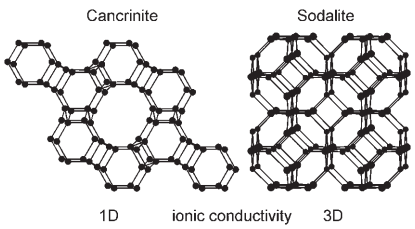
Domino reactions

Dominos on cycles: Several N-heterocycles, such as 3,4-dihydro-2*H*-1,4-benzoxazines, 1,2,3,4-tetrahydroquinoxalines, and 1,2,3,4-tetrahydroquinolines, can be obtained through a novel domino reaction mediated by triethyl phosphite under the influence of microwave irradiation (MW) in a single step from nitroaromatic compounds (see scheme).



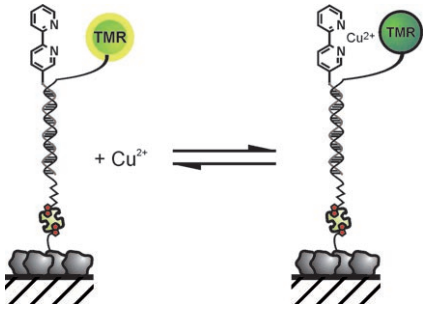
Protein Production

Quick and clean: Excellent protein yields in cell-free protein synthesis can be obtained by using polymerase chain reaction (PCR) amplified DNA templates, provided that the templates are designed for cyclization. This eliminates time-consuming cloning steps and allows one to go from complementary DNA to the protein NMR spectrum in 24 h.



Ion Transport in Zeolites

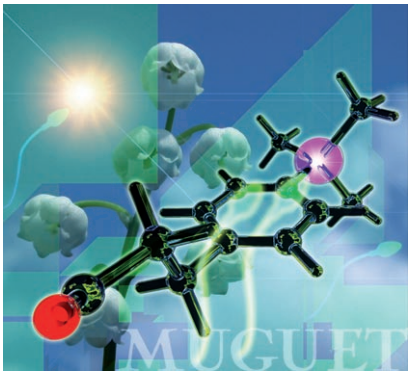
Different cation conduction mechanisms in the zeolites cancrinite and sodalite were revealed by the combination of impedance and solid-state NMR spectroscopies. Cancrinite is a one-dimensional conductor as a result of its channels, which are made up of stacked 12-rings, whereas the cation transport in sodalite takes place in three dimensions.



Single-Molecule Studies

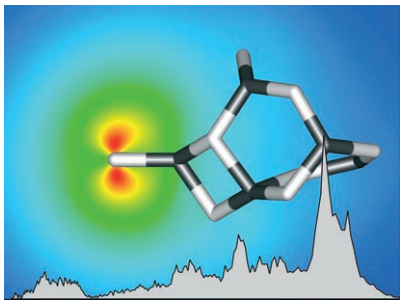
For the observation of the coordination states of individual copper(II) chelate complexes in thermodynamic equilibrium (see picture; TMR = tetramethylrhodamine), single-molecule fluorescence spectroscopy can be used. Application of time-resolved single-molecule spectroscopy opens new prospects for the investigation of reactions in the coordination sphere of metal complexes.

Contents



Sense and sensibility: Silicon analogues of the lily-of-the-valley odorants lilial and bourgeonal demonstrate that the electronic surface structure determines the interaction of an odorant with its olfactory receptor. The subtle changes in the stereoelectronic properties enable a comparison of in vivo, in vitro, and in silico data. Odor thresholds, as well as the swimming behavior of sperm cells, correlate well with the binding energies obtained from a computational model of the hOR17-4 receptor.

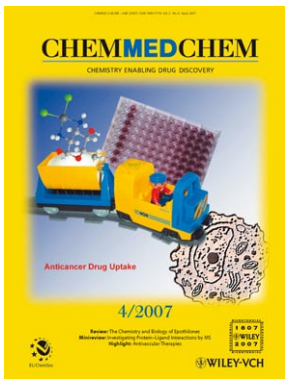
No family resemblance: IR photodissociation experiments and DFT optimizations implementing a genetic algorithm suggest that small aluminum oxide clusters have unusual structures in the gas phase. For example, the structure proposed for $[(Al_2O_3)_4]^+$ (see picture; Al black, O gray) has no features in common with bulk alumina phases.



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).

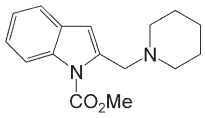
Service



For more information on ChemMedChem see www.chemmedchem.org

Corrigendum

It has been brought to the authors attention that the chemical structure for compound **11**, shown in Table 3 in their recent Communication, was incorrectly drawn. The correct structure is shown below. The authors apologize for their oversight.



11 (88 %)

Direct Synthesis of 2-(Aminomethyl)-indoles through Copper(I)-Catalyzed Domino Three-Component Coupling and Cyclization Reactions

H. Ohno,* Y. Ohta, S. Oishi, N. Fujii* _____ **2295–2298**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200604342

