Contents

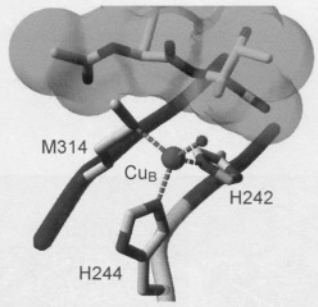
VIP ***The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:***

Obituary

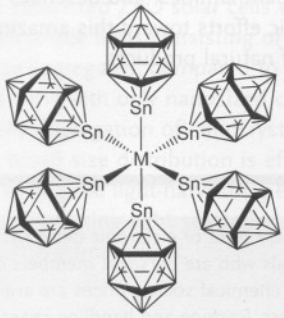
Books

Highlights

Copper at work: The aliphatic ligand hydroxylation by a copper–oxygen center has been observed for the first time on a model system of the enzyme PHM (peptidylglycine-α-hydroxylating monooxygenase). This result is put in the context of the enzymatic mechanism, which presumably involves a high-valent copper oxo unit (violet-red) that hydroxylates the substrate (cyan).



Copper Monooxygenases



Encased in stannaborates: The synthesis of the homoleptic, octahedral M^{IV} complexes $[M(SnB_{11}H_{11})_6]^{8-}$ (M = Ni, Pd, Pt) has been reported. Spectroscopic data, together with the square-planar structure obtained for the corresponding tetrakis-ligated Ni^{II} complex $[Ni(SnB_{11}H_{11})_4]^{6-}$, provide ample evidence for the extremely strong σ-donor properties of the $[SnB_{11}H_{11}]^{2-}$ ligand.

Group 10 Complexes

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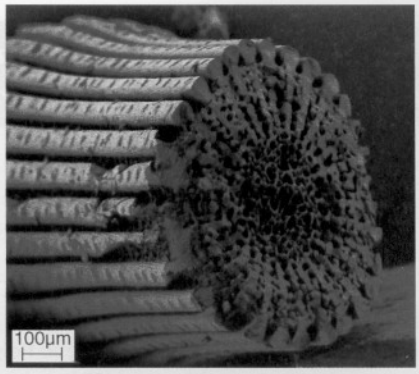
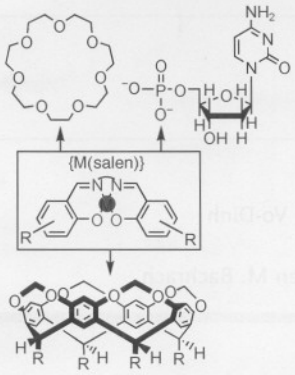


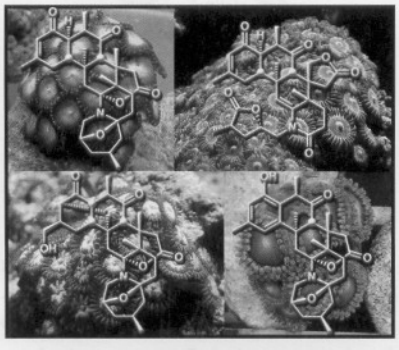
Nature is able to produce large single crystals with complex shape via amorphous precursor phases in the process of biomineralization (the picture shows an SEM image of a fracture surface of a sea urchin spicule). This strategy can be mimicked for the template synthesis of large single-crystalline materials with controllable complex shape.

Minireviews



The salens are comin': Salen synthons are becoming increasingly important for various chemical applications that go beyond their conventional use as versatile ligands in homogeneous catalysis. A recent increase in the use of these highly accessible building blocks has paved the way for the development of interesting hybrid materials with new catalytic, magnetic, and supramolecular properties.

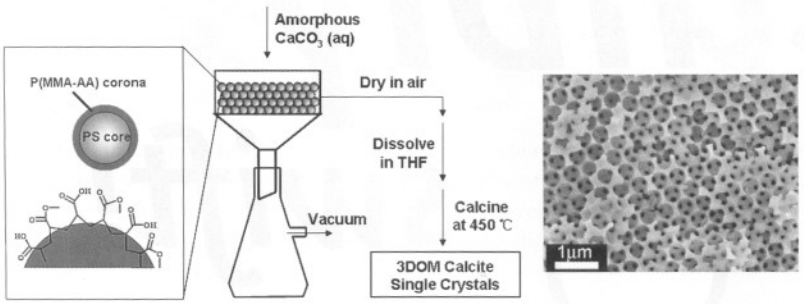
Reviews



More than meets the eye! Marine zoanthids have more to offer than stunning colors in home aquariums. They are the source of a host of fascinating natural products with great structural complexity and important biological activities. This Review chronicles the isolation and activity of zoanthamines, and describes the synthetic efforts toward this amazing class of natural products.

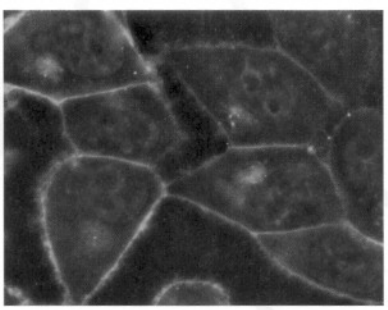
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (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.

Communications

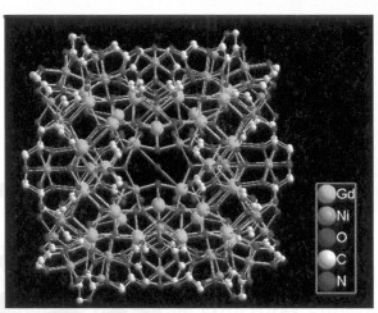


Filling the gaps: Unique 3D ordered macroporous (3DOM) calcite single crystals with controlled orientation and well-defined nanopatterns are fabricated by introducing amorphous $CaCO_3$ into a colloidal crystal template of polymer spheres (see picture). Such a bioinspired strategy suggests a route to functional single-crystalline materials and sheds light on biomineralization mechanisms.

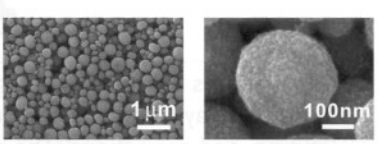
Azide imaging: A fluorogenic phosphine based on a FRET-quenching mechanism allows for live-cell imaging of azido sugars by the Staudinger ligation. This design strategy can accommodate numerous fluorophores and complementary quenchers, enabling extension to multicolor imaging. In the image shown, the nuclei are blue while the cell surfaces and Golgi are green.

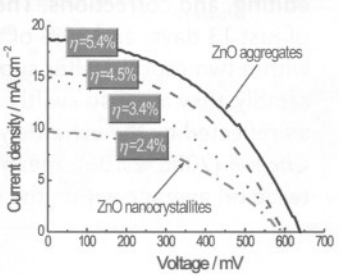


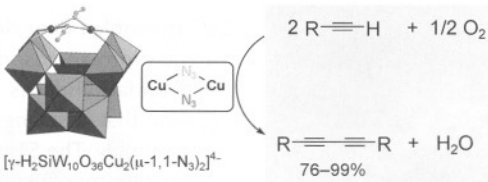
A Russian doll: A heterometallic 108-metal cluster featuring an unprecedented four-shell, nesting doll-like structure (see picture) and overall antiferromagnetic coupling is reported.



Here comes the sun: A conversion efficiency as high as 5.4% has been achieved on dye-sensitized ZnO solar cells with photoelectrode films consisting of polydisperse aggregates, compared to 2.4% for the films with only nanosized crystallites. The aggregation of nanocrystallites with a broad size distribution is effective in enhancing the light-harvesting efficiency by inducing light scattering within the photoelectrode films.

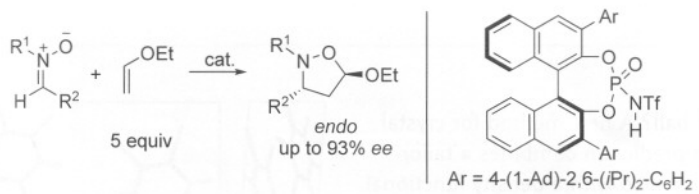






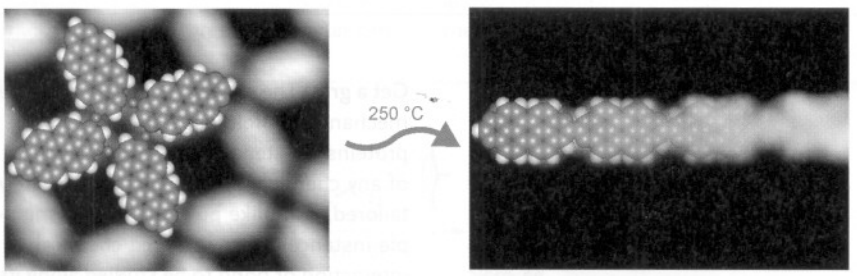
It goes on the dicopper core! A monomeric γ-Keggin silicotungstate with a dicopper core that is bridged by two μ-1,1-azido ligands catalyzes oxidative alkyne homocoupling reactions whereby various kinds of aromatic and aliphatic alkynes are selectively converted into the corresponding diynes (see picture).

Homogeneous Catalysis



Brønsted and Lewis face off: A new chiral *N*-triflyl phosphoramide is used for asymmetric 1,3-dipolar cycloaddition of diaryl nitrones to ethyl vinyl ether to give the *endo* products in up to 93% *ee* (see scheme; Tf = trifluoromethanesulfonyl; Ad = adamantyl). The structure of the chiral phosphoramide was confirmed by X-ray crystallographic analysis.

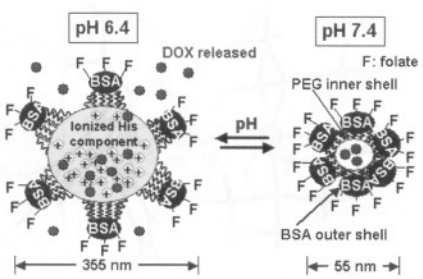
Asymmetric Synthesis



Isomerize and polymerize! Thermally induced tautomerization of the N-heteropolycyclic 1,3,8,10-tetraazaperopyrene to a Wanzlick-type carbene intermediate on a Cu(111) surface leads to covalently linked polyaromatic chains, which can be mechanically manipulated. The pictures show the respective structures superimposed on the STM images.

Surface Chemistry

Delivering the goods: A pH-sensitive nanogel consists of a hydrophobic copolymer core and two layers of hydrophilic shell (see picture). The core is loaded with a model anticancer drug, doxorubicin (DOX). The nanogel infects tumor cells in a receptor-dependent manner, kills the cells, and migrates to neighboring cells like a virus. BSA = bovine serum albumin, F = folate, PEG = polyethylene glycol.



Drug Delivery

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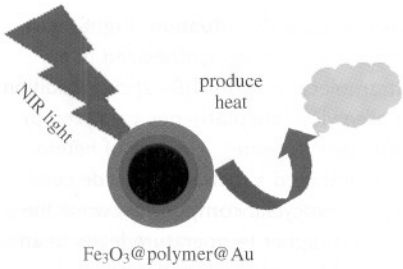
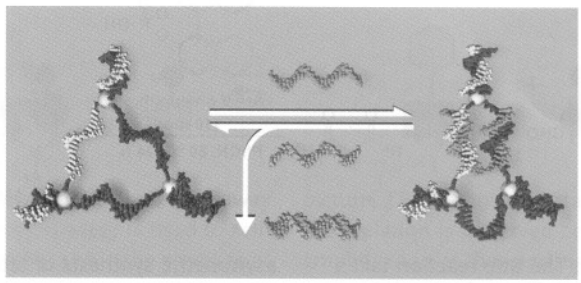


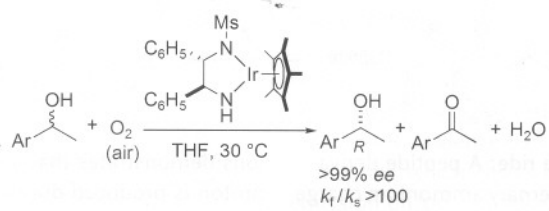
The best of both worlds: Multifunctional Fe_3O_4@polymer@Au shell nanoparticles (see scheme; Fe_3O_4 is black, polymer is blue, gold shell is brown) display good dispersibility and stability in aqueous solution. Strong magnetization and good NIR absorption are preserved in the core–shell structures. These features should facilitate biomedical applications, combining the benefits of MRI diagnosis, magnetically targeted delivery, and photothermal ablation.

Magnetic Nanoparticles



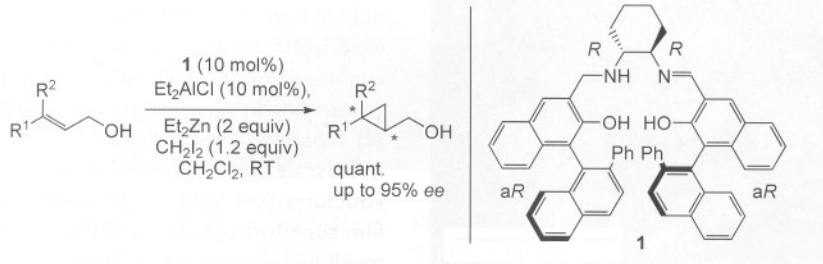
Templated metalation of DNA junctions allows incorporation of a range of transition metals into DNA assemblies. The resulting highly stable metal–DNA junctions can be assembled into dynamic multinuclear structures, with metal centers as their corners and DNA single strands as their sides. Ready and reversible structural switching of these assemblies with external agents (see picture) allows for control of geometry and metal–metal distances.

DNA Nanotechnology



Up for air: The aerobic oxidative kinetic resolution of racemic secondary alcohols with chiral bifunctional Ir, Rh, and Ru catalysts proceeds smoothly under mild conditions to provide chiral alcohols with up to 99% *ee*, and O_2 serves as an excellent hydrogen acceptor.

Aerobic Oxidation



Three angles: A highly enantioselective Simmons–Smith reaction of *trans*-disubstituted allylic alcohols was achieved by using a catalytic amount of an Al(salalen) complex at room temperature (see scheme).

Asymmetric Catalysis

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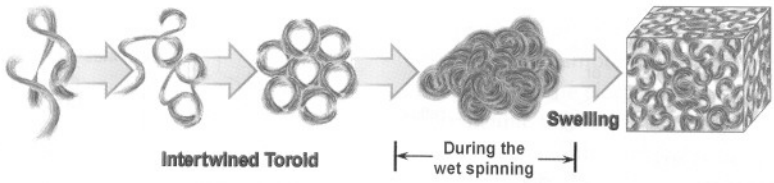
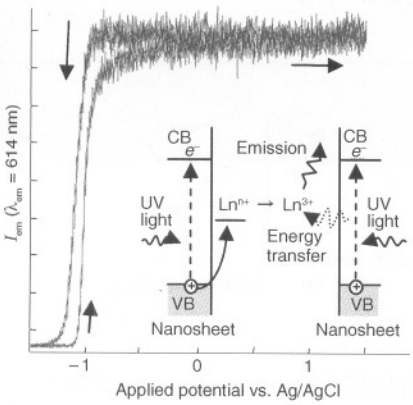


Spinning strands: A hydrogel fiber made entirely of DNA without any covalent cross-links, composed of intertwined toroid entanglements of flexible DNA strands (see scheme), was prepared by a one-step wet-spinning method with a hydrophilic ionic liquid as the condensing agent and coagulation solvent. The internal structure of the fiber was a disordered arrangement of strands with a B-DNA form. The fiber was also stable in various aqueous solutions.

DNA Structures

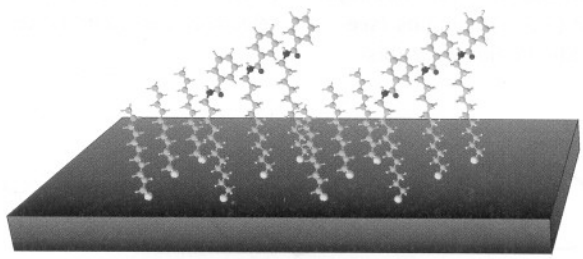
A good neighbor is better than a far-away friend: A tethering strategy is used to self-select groups that assist in the cleavage of a neighboring carboxylic ester moiety (see picture, TSA = transition-state analogue). A correlation is observed between the amplification at thermodynamic equilibrium and the catalytic efficiency.

Dynamic Selection



Getting turned on: A photoelectrochemical reaction has been used to control the photoluminescence of self-assembled nanosheet films intercalated with Ln^{3+} ions. Emission (em) occurs under anodic bias (mechanism shown) and not under cathodic bias because of the oxidation and reduction of Ln^{3+}/Ln^{n+} by holes and electrons by UV light, respectively (see picture, VB = valence band, CB = conduction band), which allows control of the emission on/off response.

Luminescence



Controlled confinement: A supramolecular approach for the design of multicomponent self-assembled monolayers on Au(111) is employed to obtain subnanometer-resolved patterns on the solid substrate (see picture). The formation of crystalline bicomponent domains is discussed in view of their potential applications in the development of new electronic devices.

Scanning Probe Microscopy

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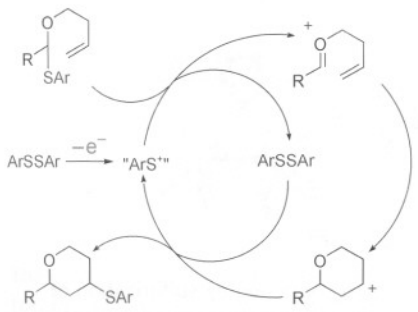


The treatment of an olefinic thioacetal with a catalytic amount of ArS(ArSSAr)-$^{+}B(C_6F_5)_4^{-}$, or the electrolysis of a mixture of an olefinic thioacetal and ArSSAr, gives rise to effective intramolecular carbon–carbon bond formation (see scheme). This transformation opens up great potential for electroinitiated cation chain reactions in organic synthesis.

Electroinitiated Reactions

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).

The issues for March 2008 appeared online on the following dates
Issue 9: February 11. · Issue 10: February 15. · Issue 11: February 22. · Issue 12: March 3

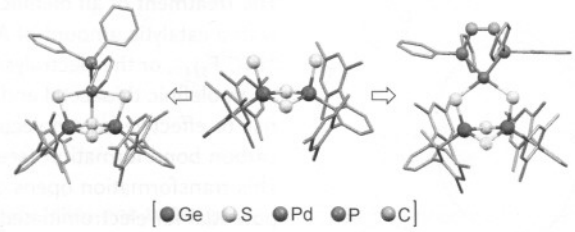
Service

Ge/Pd/S Clusters

T. Matsumoto, Y. Matsui, M. Ito, K. Tatsumi*

Synthesis of *syn*-2,4-Dimercapto-1,3,2,4-dithiadigermetane and Its Application to Ge_2PdS_4 Cluster Synthesis

Chem. Asian J.
DOI: **10.1002/asia.200700355**



Group work: *syn*-[DmpGe(SH)(μ-S)$_2$-GeDmp(SH)] (Dmp = 2,6-dimesitylphenyl) is a new entry to mercaptogermanes, synthesized from a series of polythiadigermabicyclo[*x*.1.1]alkanes (x = 3–5) obtained by sulfurization of $DmpGeH_3$ in melted elemental sulfur. The mercaptogermane is a good precursor to heteronuclear complexes composed of Ge and transition metals.

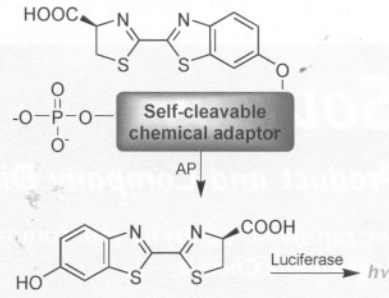
Bioluminescent Substrates

W. Zhou,* C. Andrews,* J. Liu, J. W. Shultz, M. P. Valley, J. J. Cali, E. M. Hawkins, D. H. Klaubert, R. F. Bulleit, K. V. Wood

Self-Cleavable Bioluminogenic Luciferin Phosphates as Alkaline Phosphatase Reporters

ChemBioChem
DOI: **10.1002/cbic.200700644**

After glow. Reactive chemical adaptors were used to stabilize bioluminogenic phosphates for monitoring alkaline phosphatase (AP) activity (see scheme). The 1,6-elimination based luciferin phosphate exhibited ultrasensitive ability to detect ~10^{-22} mol of AP enzyme in a homogeneous solution, and picograms of protein in an immunoassay.

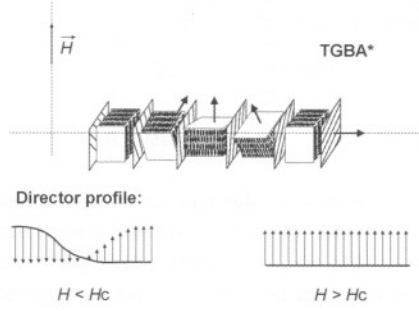


Liquid Crystals

V. Domenici,* C. A. Veracini, V. Novotná, R. Y. Dong

Twist Grain Boundary Liquid-Crystalline Phases under the Effect of the Magnetic Field: A Complete ^2H and ^{13}C NMR Study

ChemPhysChem
DOI: **10.1002/cphc.200700647**



Magnetic twist: A complete ^2H and ^{13}C NMR study on a wide range of TGBA* and TGBC* phases reveals a peculiar effect of the external magnetic field in winding and deforming the TGB supramolecular structure (see picture).

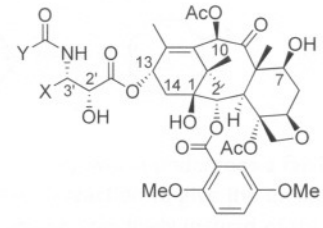
QSAR Studies

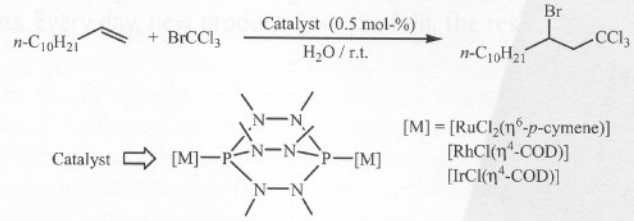
R. P. Verma,* C. Hansch

Taxane Analogues against Breast Cancer: A Quantitative Structure–Activity Relationship Study

ChemMedChem
DOI: **10.1002/cmdc.200700278**

Revealing relationships: Quantitative structure–activity relationships were developed for four series of taxane derivatives with respect to their inhibitory activities against breast cancer cells. The activities of these taxane derivatives are largely dependent either on their hydrophobicity or the hydrophobic/molar refractivity descriptor of their substituents.





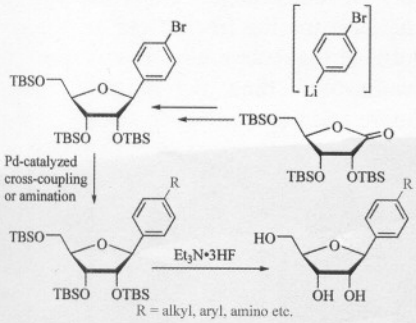
The novel dinuclear complexes $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-THDP})]$ and $[\{MCl(\eta^4cod)\}_2(\mu\text{-THDP})]$ (M = Rh, Ir), containing the bridging ligand tris(1,2-dimethylhydrazino)diphosphane (THDP), have been synthesized and used as catalysts in the atom-transfer radical addition of bromotrichloromethane to olefins (Kharasch reaction) in aqueous media.

Kharasch Reaction

A. E. Díaz-Álvarez, P. Crochet,* M. Zablocka,* C. Duhayon, V. Cadierno, J.-P. Majoral*

Developing the Kharasch Reaction in Aqueous Media: Dinuclear Group 8 and 9 Catalysts Containing the Bridging Cage Ligand Tris(1,2-dimethylhydrazino)diphosphane

Eur. J. Inorg. Chem.
DOI: **10.1002/ejic.200701132**



A modular and efficient synthesis of a series of diverse 4- and 3-substituted benzene and aniline C-ribonucleosides was developed on the basis of Pd-catalyzed cross-coupling and amination reactions of protected bromophenyl C-nucleosides.

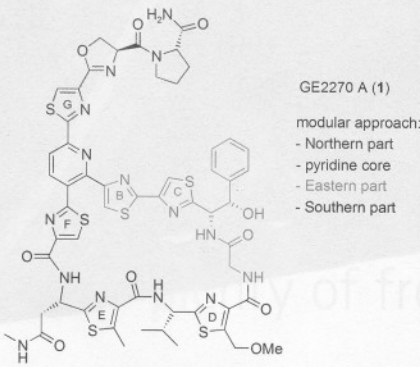
Benzene C-Ribonucleosides

M. Štefko, R. Pohl, B. Klepetářová, M. Hocek*

A Modular Methodology for the Synthesis of 4- and 3-Substituted Benzene and Aniline C-Ribonucleosides

Eur. J. Org. Chem.
DOI: **10.1002/ejoc.200701168**

A modular assembly of the individual thiazole fragments to the central pyridine core was achieved by regioselective cross-coupling reactions giving access to the title compound (see graphic) in an overall yield of 4.8% over 20 steps. The successful implementation of orthogonal metalation and protecting group strategies further contributed to the brevity of the total synthesis.



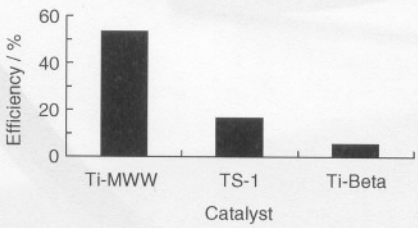
Antibiotics

O. Delgado, H. M. Müller, T. Bach*

Concise Total Synthesis of the Thiazolyl Peptide Antibiotic GE2270 A

Chem. Eur. J.
DOI: **10.1002/chem.200701823**

Ti time for dioxane: Oxidation of 1,4-dioxane with aqueous H_2O_2 over various titanosilicates was investigated. Use of Ti-MWW as catalyst leads to much higher conversions than with TS-1 and Ti-Beta under solvent-free conditions and is accounted for by a radical mechanism. The number of active intermediate Ti species is highly dependent on the substrate, solvent, and titanosilicate used.

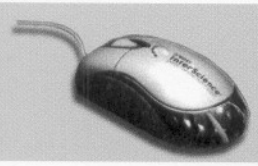


Heterogeneous Catalysis

W. Fan, Y. Kubota, T. Tatsumi*

Oxidation of 1,4-Dioxane over Ti-MWW in the Presence of H_2O_2

ChemSusChem
DOI: **10.1002/cssc.200700003**



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