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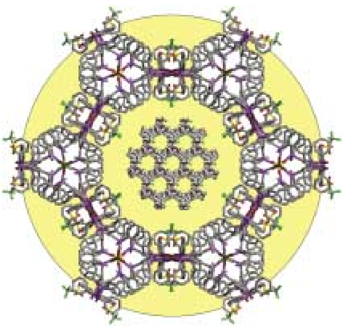
COVER PICTURE

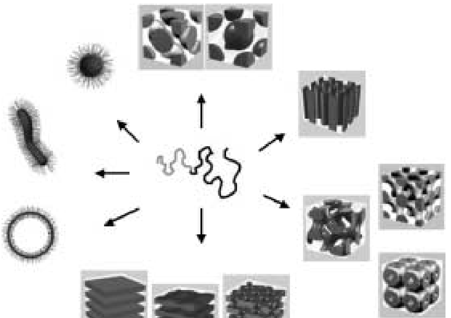
The cover picture shows an unusually wide (16 Å) channel in a stable nanoporous coordination framework, which is also novel in being based on bridging phosphane ligands. A space-filling representation of a segment of the structure is shown at the center of the picture. The as-synthesized material contains disordered ethanol guests, which can be exchanged for other solvents, and subsequently the material was obtained virtually guest-free, without structural collapse. The unconventional use of a phosphane enabled information to be gained on this framework's solution-based precursors (by ^{31}P NMR spectroscopy) which appear to be discrete coordination cages. Further details are reported by S. L. James and co-workers on p. 764 ff.



REVIEWS

Contents

A large number of superstructures with characteristic dimensions in the range of a few nanometers up to several micrometers are formed by the self-organization of block copolymers (see picture). Possible applications in the fields of materials science and molecular biology are currently being intensively investigated. Their range of application extends from the production of inorganic nanoparticles and mesoporous materials up to take-up/release systems in chemo- and gene therapy.



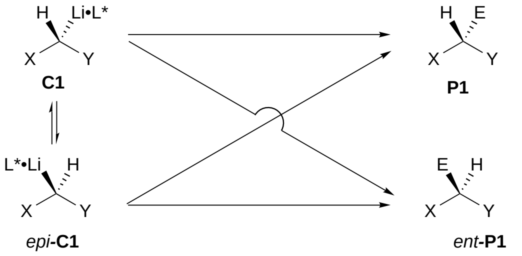
Angew. Chem. **2002**, *114*, 712–739

S. Förster,* T. Plantenberg 688–714

From Self-Organizing Polymers to Nanohybrid and Biomaterials

Keywords: amphiphiles · hybrid materials · nanostructures · polymers · self-organization

Chiral organolithium compounds are versatile intermediates with numerous applications in asymmetric synthesis. They range widely in their configurational stability and in the stereochemistry of their electrophilic substitution. Effective transfer of stereochemical information from the lithiated intermediate (**C1** and *epi*-**C1**) to the final product (**P1** and *ent*-**P1**) is dependent on the interplay between these two factors.



Angew. Chem. **2002**, *114*, 740–763

A. Basu,* S. Thayumanavan* . 716–738

Configurational Stability and Transfer of Stereochemical Information in the Reactions of Enantioenriched Organolithium Reagents

Keywords: asymmetric synthesis · configuration determination · electrophilic substitution · enantioselectivity · lithium

ESSAY

Has translation a central role in the present and future of science? After showing the importance of translating in the past, in the way the names of the chemical elements were transferred (from Dutch sources) to Japanese, the author tries to answer the above question. His conclusion is that today's dominance of English imposes an increased need for translation, as 1) the major portion of the secondary literature in any country is published in that nation's language, 2) in cases where English is the destination language for publication, scientists in many non-English speaking nations report their primary research in their mother tongue and then have to translate their results into English for submission, and 3) research has to be communicated to non-scientists, including the public, the mass media, educators, political leaders, and other decision makers.

Angew. Chem. **2002**, *114*, 765–768

S. L. Montgomery* 739–742

Chemical Transformations: Translation and the Periodic Table in Japan

Keywords: history of science · periodic table · translation

VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Enantioselective Synthesis of the Kedarcidin Chromophore Aglycon in a Differentially Protected Form	A. G. Myers,* P. C. Hogan, A. R. Hurd	◆
Surface Structure and Crystal Growth in Zeolite Beta C	B. Slater,* R. A. Catlow, Z. Liu, T. Ohsuna, O. Terasaki, M. A. Camblor	
Semiconductor Nanohelices Templated by Supramolecular Ribbons	E. D. Sone, E. R. Zubarev, S. I. Stupp*	
Phase-Sensitive Supramolecular Chirogenesis in Bisporphyrin Systems	V. V. Borovkov,* T. Harada, Y. Inoue, R. Kuroda*	
The Stable Pentamethylcyclopentadienyl Cation	J. B. Lambert,* L. Lin, V. Rassolov	
Polymeric Surfactants for the New Millennium: A pH-Responsive, Zwitterionic, Schizophrenic Diblock Copolymer	S. Liu, S. P. Armes*	

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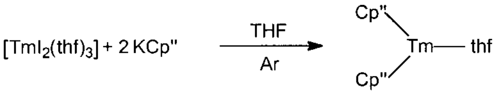
HIGHLIGHTS

That previously unattainable organolanthanide(II) complexes may be accessible through judicious manipulation of reaction conditions and supporting ligands is suggested by the recent isolation of the organothulium(II) compound $[\mathrm{Cp''_2Tm(thf)}]$ [Eq. (1); $\mathrm{Cp''} = \eta^5\text{-}C_5H_3\text{-1,3-}(SiMe_3)_2$]. In light of the diverse reactions mediated by Sm^{II} compounds it seems likely that these new compounds will provide a useful addition to the armory of reagents available to the synthetic chemist.

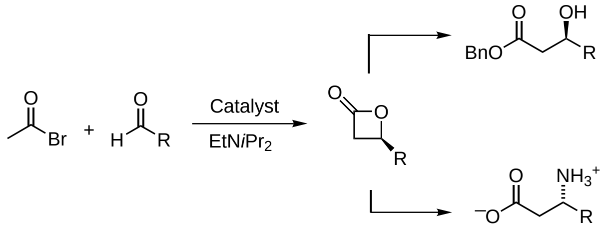


(1)

Angew. Chem. **2002**, *114*, 769 – 770

Keywords: cyclopentadienyl ligands · dysprosium · lanthanides · metallocenes · thulium

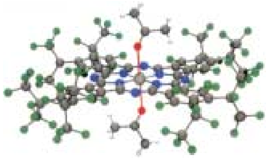
Owing to their highly strained ring system and interesting functional group, β-lactones possess significant synthetic potential. Recently, novel methods have been developed to synthesize these valuable building blocks very efficiently by catalytic, enantioselective reactions, such as [2+2] cycloadditions, starting from simple precursors. These processes also offer an attractive alternative for the synthesis of optically active β-hydroxy and β-amino acids (see scheme).



Angew. Chem. **2002**, *114*, 771 – 772

Keywords: asymmetric catalysis · cycloaddition · lactones · small ring systems

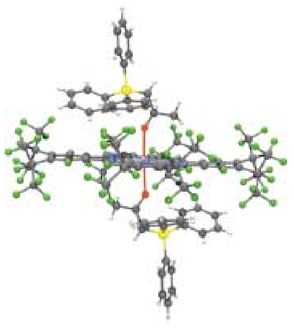
COMMUNICATIONS



A higher anticancer activity is observed in photodynamic tests with the first sterically bulky (nonplanar) perhalogenated zinc phthalocyanine (Pc), $[F_{64}PcZn(acetone)_2]$ (see structure: F green, N blue, O red, C gray) in comparison with planar zinc perfluorophthalocyanine. The perfluoroisopropyl substituents enhance the solubility, stabilize axial ligands (such as the coordinated acetone molecules in the structure shown), narrow the HOMO – LUMO gap, shift redox potentials, and increase the lifetime of the excited triplet state of the new complex.

Angew. Chem. **2002**, *114*, 773 – 776

Keywords: fluorinated ligands · photodynamic therapy · phthalocyanines · zinc

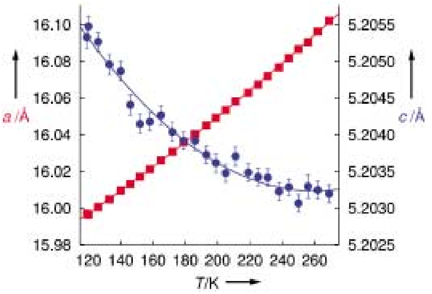


An enzyme-inspired phthalocyanine (Pc) complex $[F_{64}PcCo(acetone)_2]$ is the first representative of a novel class of robust homogeneous catalysts. This complex couples aryl and alkyl phosphanes with acetone to catalytically produce ylides (the structure shows the ylide coordinated to the $F_{64}PcCo$ unit: F green, N blue, O red, C gray, P yellow) and water under ambient conditions using only air, a route that avoids the classical use of halogenated intermediates.

Angew. Chem. **2002**, *114*, 776 – 780

Keywords: cobalt · fluorinated ligands · homogeneous catalysis · phthalocyanines · ylides

A helix that expands on cooling: The crystal structure of TrpGly · H_2O consists of helical peptide nanotubes extending throughout the crystal. The thermal expansion is negative in the helical direction (see graph; *a* axis: red, *c* axis: blue). This effect is believed to be linked to the increasing order of water molecules enclosed in the helices.



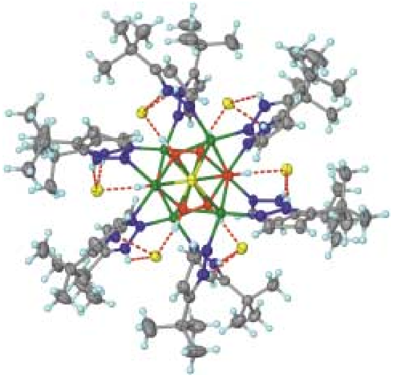
Angew. Chem. **2002**, *114*, 780–782

H. Birkedal,* D. Schwarzenbach,
P. Pattison 754–756

Observation of Uniaxial Negative Thermal Expansion in an Organic Crystal

Keywords: crystal engineering · helical structures · hydrogen bonds · peptides · X-ray diffraction

An unusual vertex-shared double-cubane $[\{Cu_3(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3\}_2Cu]^{6+}$ core surrounded by a belt of hydrogen-bonded chloride ions is present in the title compound. Magnetic data show an $S = 1/2$ ground state, which implies there is substantial spin-frustration within the hepta-copper aggregate.



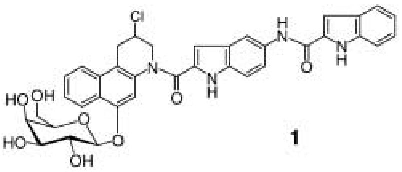
Angew. Chem. **2002**, *114*, 782–784

X. Liu, J. A. McAllister,
M. P. de Miranda, B. J. Whitaker,
C. A. Kilner, M. Thornton-Pett,
M. A. Halcrow* 756–758

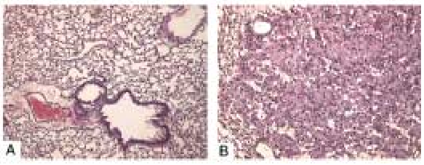
Supramolecular Templating of the Double-Cubane $[\{Cu_3(Hpz^{tBu})_6(\mu_3\text{-}Cl)\text{-}(\mu_3\text{-}OH)_3\}_2Cu]Cl_6$ (Hpz^{tBu} = 5-*tert*-Butylpyrazole)

Keywords: cluster compounds · copper · hydrogen bonds · magnetochemistry · N ligands

Perfectly adept for tumor treatment: With the seco-CBI-Q galactoside **1** a novel highly potent prodrug for the selective treatment of cancer using the ADEPT approach was developed, which shows very promising results in preclinical trials on a human bronchial carcinoma in SCID mice (see picture; lung tissue after (A) and before treatment (B)).



1



Angew. Chem. **2002**, *114*, 785–787

L. F. Tietze,* T. Feuerstein, A. Fecher,
F. Haunert, O. Panknin, U. Borchers,
I. Schuberth, F. Alves 759–761

Proof of Principle in the Selective Treatment of Cancer by Antibody-Directed Enzyme Prodrug Therapy: The Development of a Highly Potent Prodrug

Keywords: ADEPT · antitumor agents · enzymes · glycosides · monoclonal antibodies · prodrugs

α-Helical L- and D-polyalanines have magnetic properties when self-assembled as monolayers on gold surfaces. The properties depend on the chirality of the molecules and on the direction of their dipole moment relative to the substrate. They were investigated by IR spectroscopy, which determined the orientation of the molecules relative to the surface in the presence of a magnetic field, and by measuring the spin selectivity for electron transmission through the layers.

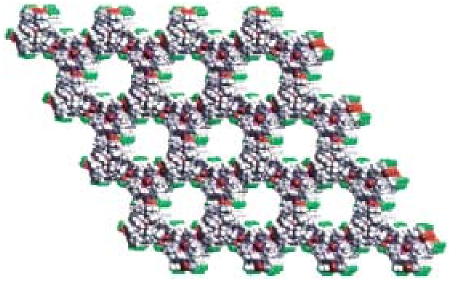
Angew. Chem. **2002**, *114*, 787–790

I. Carmeli, V. Skakalova, R. Naaman,*
Z. Vager 761–764

Magnetization of Chiral Monolayers of Polypeptide: A Possible Source of Magnetism in Some Biological Membranes

Keywords: chirality · electron transport · magnetic properties · monolayers · peptides

No interpenetration: The use of bulky phosphane ligands allows the preparation of a non-interpenetrating two-dimensional nanoporous structure with hexagonal channels (see picture). In the as-synthesized polymer these channels are saturated with solvent, however, this solvent can be exchanged for other solvents which in turn can be removed by heating under vacuum without collapse of the structure.



Angew. Chem. **2002**, *114*, 790–793

X. Xu, M. Nieuwenhuyzen,
S. L. James* 764–767

A Nanoporous Metal–Organic Framework Based on Bulky Phosphane Ligands

Keywords: crystal engineering · host–guest systems · nanostructures · phosphane ligands · polymerization · silver

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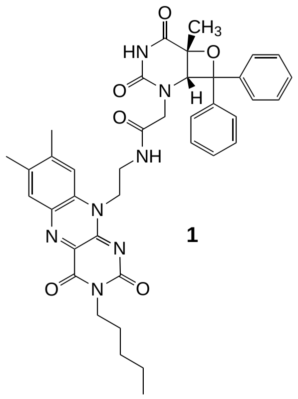
Photolyase-catalyzed repair of pyrimidine (6-4) photoadducts was modeled with synthetic, covalently linked flavin–oxetane **1**. The repair reaction (oxetane splitting) requires the reduced flavin in its deprotonated form. The key step of the repair reaction involves an electron transfer from the flavin to the oxetane.



1

Angew. Chem. **2002**, *114*, 793–796

M. K. Cichon, S. Arnold,
T. Carell* 767–770

A (6-4) Photolyase Model: Repair of DNA (6-4) Lesions Requires a Reduced and Deprotonated Flavin

Keywords: bioorganic chemistry · DNA · DNA repair · mutagenesis · photolyase

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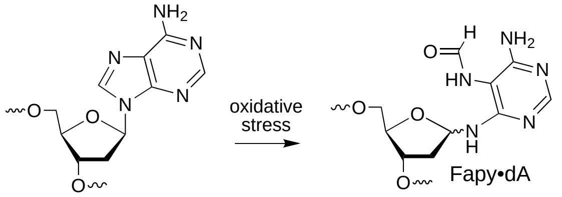
Formamidopyrimidine lesions (Fapy·dA; see scheme) are produced in greater yields than 8-oxopurines (OA) under O_2-deficient conditions from a common intermediate. OA give rise to low levels of A→C transversions. In vitro experiments show that Fapy·dA induces a DNA polymerase to misinsert nucleotides significantly more often than does OA, which suggests that the formamidopyrimidine may be a more potent premutagenic lesion.



Angew. Chem. **2002**, *114*, 797–799

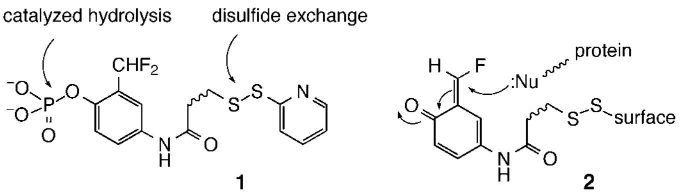
M. O. Delaney, C. J. Wiederholt,
M. M. Greenberg* 771–773

Fapy·dA Induces Nucleotide Misincorporation Translesionally by a DNA Polymerase

Keywords: bioorganic chemistry · DNA · DNA damage · DNA polymerase · mutagenesis

---

Disulfide exchange leads to the attachment of phosphate ester **1** to a solid surface, which can then be used in turnover selection to screen a large library of proteins for phosphate monoester hydrolysis activity. This ester hydrolysis leads to formation of an electrophilic quinone methide **2**, which bonds covalently to the protein catalyst and links it to the surface for selection.



1 **2**

Angew. Chem. **2002**, *114*, 801–803

J. R. Betley, S. Cesaro-Tadic,
A. Mekhalfia, J. H. Rickard, H. Denham,
L. J. Partridge, A. Plückthun,*
G. M. Blackburn* 775–777

Direct Screening for Phosphatase Activity by Turnover-Based Capture of Protein Catalysts

Keywords: biosensors · catalytic antibodies · enzyme catalysis · inhibitors · phosphatases

Blocking the catalyst through the formation of $Rh^I-\eta^6$-arene complexes (the complex $[Rh((R,R)$-Et-DuPHOS$)(C_6H_6)]^+$ is shown; Et-DuPHOS = 2′,5′,2″,5″-tetraethyl-1,2-bis(phospholanyl)benzene) can decrease the activity of asymmetric hydrogenations. The inhibiting effects of aromatic compounds were quantified by means of kinetic measurements and confirmed by means of X-ray crystal structure analysis and ^{103}Rh NMR spectroscopy.

Angew. Chem. **2002**, *114*, 814–817

D. Heller,* H.-J. Drexler,
A. Spannenberg, B. Heller, J. You,
W. Baumann* 777–780

The Inhibiting Influence of Aromatic Solvents on the Activity of Asymmetric Hydrogenations

Keywords: arene ligands · asymmetric catalysis · hydrogenation · NMR spectroscopy · rhodium

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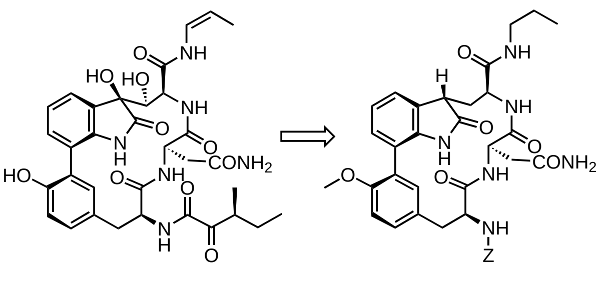
Based on information from the X-ray structure of the TMC-95A/proteasome complex, TMC-95A (**A**) was reduced to the minimum core structure (**B**). The inhibitory potency of the synthetic analogue confirms that the simplified ring structure may well serve as the lead for further improvement of affinity and selectivity of reversible proteasome inhibitors.



A **B**

Angew. Chem. **2002**, *114*, 817–820

M. Kaiser, M. Groll, C. Renner,
R. Huber, L. Moroder* 780–783

The Core Structure of TMC-95A Is a Promising Lead for Reversible Proteasome Inhibition

Keywords: inhibitors · natural products · NMR spectroscopy · structure–activity relationships · total synthesis

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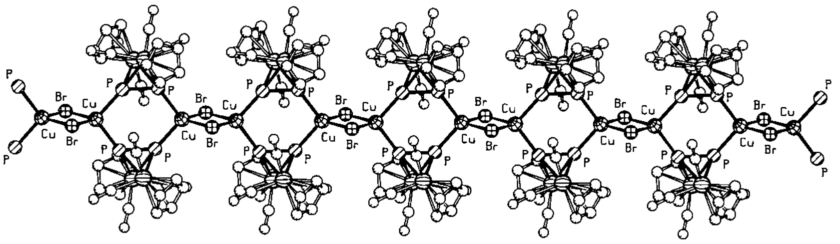
Bridging coordination of Mo_2P_2 complexes between metal centers is a prerequisite for the formation of a one-dimensional polymer. The choice of counterion also has a deciding role in determining the polymer structure: while the complex $[Cp_2Mo_2(CO)_4(\mu,\eta^2-P_2)]$ (**1**; $Cp = C_5H_5$) with $AgNO_3$ forms a zigzag polymer chain, with CuBr **1** forms a linear coordination polymer (see structure).



Angew. Chem. **2002**, *114*, 820–823

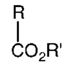
J. Bai, E. Leiner, M. Scheer* .. 783–786

P_2-Ligand Complexes as Building Blocks for the Formation of One-Dimensional Polymers

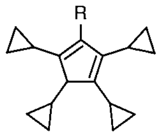
Keywords: coordination polymers · copper · molybdenum · P ligands · silver

Accessible in one step each, tetra- and pentacyclopropylcyclopentadiene (**3**) can be prepared from dicyclopropylacetylene (**1**) and *n*-butyl formate (**2a**) or methyl cyclopropanecarboxylate (**2b**), respectively. The five cyclopropyl substituents in **3b** exert a significant donor effect on the cyclopentadienide core when this is bound to a metal center such as in **4**.

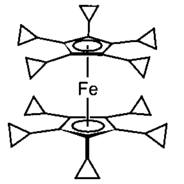

1


RCO_2R'

2a: R = H, R' = *n*Bu
2b: R = *c*Pr, R' = Me



3a: R = H
3b: R = *c*Pr



4

Angew. Chem. **2002**, *114*, 811 – 814

I. Emme, S. Redlich, T. Labahn, J. Magull, A. de Meijere* . . . . 786 – 789

Tetra- and Pentacyclopropylcyclopentadiene—Two New Donor-Substituted Ligands for Metal Complexes

Keywords: carbocations · cyclopentadienyl ligands · hydrocarbons · metallocenes · substituent effects

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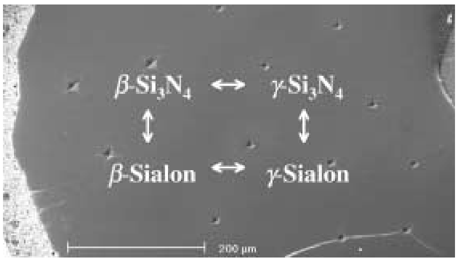

Excellent mechanical properties make $\gamma\text{-Si}_2\text{AlON}_3$, one of the first spinel sialons and 4-3-spinels, a promising material for structural and abrasive applications. The hardness of this phase synthesized at 13 GPa/1800°C surpasses that of the low-pressure α- and β-sialons, which are used for metal-cutting and engineering applications. The picture shows a $\gamma\text{-Si}_2\text{AlON}_3$ surface that was used for Vickers hardness testing and indicates the structural relation between β- and γ-sialons and the corresponding phases of Si_3N_4.

Angew. Chem. **2002**, *114*, 804 – 808

M. Schwarz,* A. Zerr, E. Kroke,* G. Miehe, I-W. Chen, M. Heck, B. Thybusch, B. T. Poe, R. Riedel . . . . 789 – 793

Spinel Sialons

Keywords: ceramics · high-pressure chemistry · oxide nitrides · sialons · spinel phases

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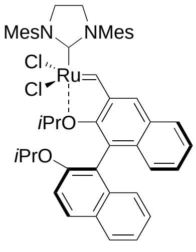
A bulky binol-based ligand is the key structural feature of the ruthenium complex **1**, which displays an unprecedented metathesis activity combined with high stability. For a range of dienes, ring-closing metathesis reactions catalyzed by **1** lead to near quantitative yields of cycloalkenes after a few minutes.



1

Angew. Chem. **2002**, *114*, 832 – 834

H. Wakamatsu, S. Blechert* . . 794 – 796

A Highly Active and Air-Stable Ruthenium Complex for Olefin Metathesis

Keywords: biaryls · carbene ligands · metathesis · O ligands · ruthenium

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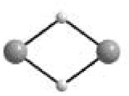

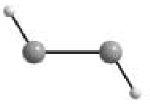

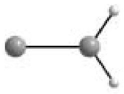

The five binary species Ga(μ-H)$_2$Ga, In(μ-H)$_2$In (see left structure), HGaGaH, HInInH (center), and $GaGaH_2$ (right) were prepared by matrix isolation and characterized unambiguously by IR spectroscopy and quantum-chemical calculations. Investigations of the photochemical properties reveal that each of the isomers can be interconverted by photolysis.

Angew. Chem. **2002**, *114*, 829 – 832

H.-J. Himmel,* L. Manceron, A. J. Downs, P. Pullumbi . . . . . . 796 – 799

Characterization and Photochemistry of the Gallium and Indium Subhydrides Ga_2H_2 and In_2H_2

Keywords: gallium · hydrides · indium · matrix isolation · photochemistry

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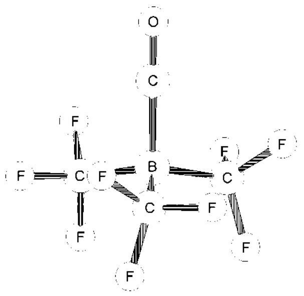
By hydrolysis of a single CF_3 group in concentrated sulfuric acid, the new boron carbonyl $(CF_3)_3B{-}CO$ compound (see molecular structure) is obtained from $K[B(CF_3)_4]$. $(CF_3)_3B{-}CO$ exhibits rather unusual properties and bears an electrophilic carbonyl carbon atom.



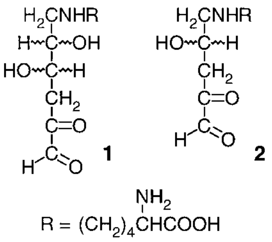
Angew. Chem. **2002**, *114*, 823 – 825

A. Terheiden, E. Bernhardt, H. Willner,* F. Aubke* . . . . 799 – 801

Carbonyltris(trifluoromethyl)borane, $(CF_3)_3BCO$, An Unusual Boron Carbonyl

Keywords: ab initio calculations · boranes · carbonyl ligands · IR spectroscopy

The novel dideoxyosones 1 and 2 were shown to be precursors of the important in vivo crosslinks glucosepane and pentosidine. In **1** and **2**, the lysine N^{ε} atom is directly bonded to C1 of the original sugar group. The formation of these compounds proceeds through carbonyl shifts along the entire carbohydrate backbone.



Angew. Chem. **2002**, *114*, 826–828

K. M. Biemel, J. Conrad,
M. O. Lederer* 801–804

Unexpected Carbonyl Mobility in Aminoketoses: The Key to Major Maillard Crosslinks

Keywords: carbohydrates · heterocycles · Maillard reaction · protein cross-linking · structure elucidation

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ARTS in chemistry: Aryloxymethyl hyponitrites provide the first aryloxyl radical thermal sources (**ARTS**) which generate a well-defined flux of aryloxyl radicals ($ArO^{\bullet}$) at room temperature [Eq. (1)]. These novel compounds can be used for quantitative studies on reactions of $ArO^{\bullet}$ with biomolecules, as exemplified by the $PhO^{\bullet}$-mediated oxidation of human low-density lipoprotein.

$$\underset{\textbf{(ARTS)}}{[ArOCH_2ON]_2} \xrightarrow{(23^{\circ}C,\ t_{1/2} \approx 70\ min)} ArO^{\bullet} + H_2C{=}O \qquad (1)$$

Angew. Chem. **2002**, *114*, 808–811

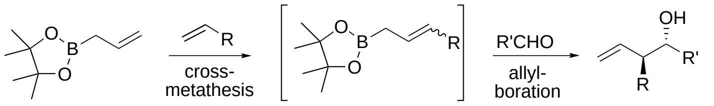
T. Paul,* K. U. Ingold* 804–806

A Method for Thermal Generation of Aryloxyl Radicals at Ambient Temperatures: Application to Low-Density Lipoprotein (LDL) Oxidation

Keywords: azo compounds · lipoproteins · oxidation · radicals · vitamins

---

Reactive reagents can be prepared by means of olefin cross-metathesis. A wide variety of functionalized allyl boronates were synthesized and were found to react cleanly with aldehydes to afford homoallylic alcohols, without prior purification (see scheme). Olefins that bear allylic ethers, halides, protected aldehydes, and sterically encumbering groups are viable substrates for this reaction.



Angew. Chem. **2002**, *114*, 835–838

S. D. Goldberg, R. H. Grubbs* 807–810

A One-Pot Cross-Metathesis/Allylboration Reaction: A Three-Component Coupling for the Synthesis of Functionalized Homoallylic Alcohols

Keywords: allylation · boranes · chemoselectivity · cross-coupling · metathesis

---

When four conditions are met redox polymers can be electrodeposited by ligand exchange: the film must be electron- or hole-conducting; the redox centers of the deposited polymer that are based on transition metal complexes must contain a labile ligand in their inner coordination sphere; the redox polymer must contain a strongly coordinating but yet uncoordinated ligand; and the surface density of the adsorbed redox polymer must be high. By taking care of these points, the authors also succeeded in co-depositing enzymes and electroreducing/oxidizing their substrates with the electrodes obtained.

Angew. Chem. **2002**, *114*, 838–841

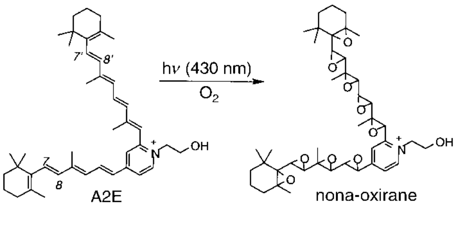
Z. Gao, G. Binyamin, H.-H. Kim,
S. C. Barton, Y. Zhang,
A. Heller* 810–813

Electrodeposition of Redox Polymers and Co-Electrodeposition of Enzymes by Coordinative Crosslinking

Keywords: biosensors · chelates · electrochemistry · polymerization · redox chemistry

---

Nine epoxide rings are formed sequentially when A2E is irradiated with blue light in the presence of oxygen [Eq. (1)]. Mechanistically, A2E generates singlet oxygen and reacts with it to give the polyoxiranes. An understanding of the reaction of A2E with oxygen is important as blue light induces the apoptotic death of A2E-laden retinal pigment epithelium cells, which are typical of age-related macular degeneration.



(1)

Angew. Chem. **2002**, *114*, 842–845

S. Ben-Shabat, Y. Itagaki, S. Jockusch,
J. R. Sparrow,* N. J. Turro,*
K. Nakanishi* 814–817

Formation of a Nonaoxirane from A2E, a Lipofuscin Fluorophore related to Macular Degeneration, and Evidence of Singlet Oxygen Involvement

Keywords: heterocycles · macular degeneration · peroxides · photochemistry · singlet oxygen

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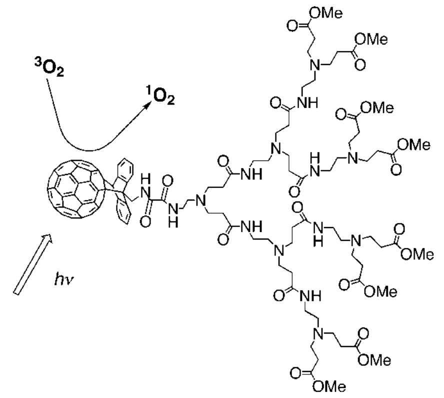
Reversible Diels–Alder reaction of C_{60} with an anthracenyl dendron bearing a poly(amidoamine) substituent forms the fullerodendrimer depicted. It is readily soluble in water and acts as a photosensitizer for the generation of singlet oxygen.



Angew. Chem. **2002**, *114*, 845–847

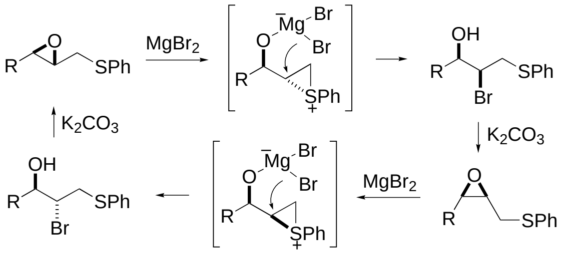
Y. Takaguchi,* T. Tajima, K. Ohta, J. Motoyoshiya, H. Aoyama, T. Wakahara, T. Akasaka,* M. Fujitsuka, O. Ito* 817–819

Reversible Binding of C_{60} to an Anthracene Bearing a Dendritic Poly(amidoamine) Substituent to give a Water-Soluble Fullerodendrimer

Keywords: cycloaddition • dendrimers • fullerenes • photochemistry • singlet oxygen

---

A double inversion of configuration and episulfonium ion intermediates are at the heart of a method for the stereospecific interconversion between *cis* and *trans* 2,3-epoxysulfides (see scheme). This method can be used in the stereoselective synthesis of epoxides.



Angew. Chem. **2002**, *114*, 847–849

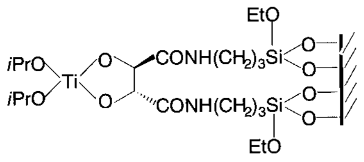
A. Hirai, T. Tonooka, K. Wakatsuki, K. Tanino, M. Miyashita* 819–821

Stereospecific Interconversion between *cis* and *trans* 2,3-Epoxysulfides

Keywords: bromohydrins • epoxidation • isomerization • nucleophilic substitution • synthetic methods

---

A heterogeneous version of the Sharpless epoxidation: a chiral tartaric acid derivative is grafted onto the surface of silica and in the mesopores of MCM-41 (see picture). The hybrid chiral catalyst is as effective as the homogeneous complex in terms of turnover number and enantioselectivity, and the product is easily separated by simple filtration.



Angew. Chem. **2002**, *114*, 849–852

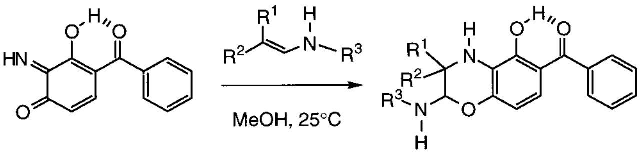
S. Xiang, Y. Zhang, Q. Xin, C. Li* 821–824

Asymmetric Epoxidation of Allyl Alcohol on Organic–Inorganic Hybrid Chiral Catalysts Grafted onto the Surface of Silica and in the Mesopores of MCM-41

Keywords: alcohols • allylic compounds • asymmetric catalysis • epoxidation • heterogeneous catalysis • synthetic methods

---

The regiospecific cycloaddition of an *o*-quinone imine and a highly reactive enamine, which are electrogenerated simultaneously, can be carried out at ambient temperature in the absence of catalyst. This reaction is a powerful tool for the one-pot synthesis of new polyfunctionalized 1,4-benzoxazine derivatives (see scheme).



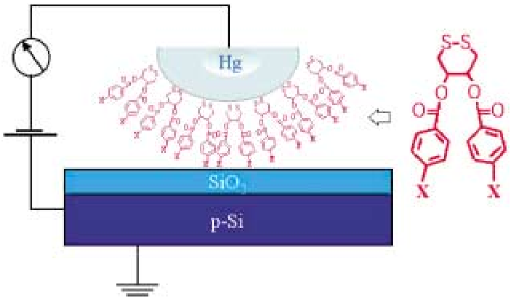
Angew. Chem. **2002**, *114*, 852–855

M. Largeron,* A. Neudorffer, M. Vuilhorgne, E. Blattes, M.-B. Fleury 824–827

Regiospecific Inverse-Electron-Demand Diels–Alder Reaction of Simultaneously Electrogenerated Diene and Dienophile: An Expeditious Route to Polyfunctionalized 1,4-Benzoxazine Derivatives

Keywords: cofactors • cycloaddition • electrochemistry • nitrogen heterocycles • quinones • synthetic methods

Junction function: Molecule-controlled devices based on metal–semiconductor junctions can exhibit negative differential resistance (NDR) at room temperature. The active component is a self-assembled monolayer of molecular dipoles (see schematic representation; X = CF_3, CN, H, OMe). A systematic change in the dipole moment of these molecules results in a corresponding systematic change in the NDR effect, thus establishing for the first time molecularly tunable NDR.



Angew. Chem. **2002**, *114*, 855–858

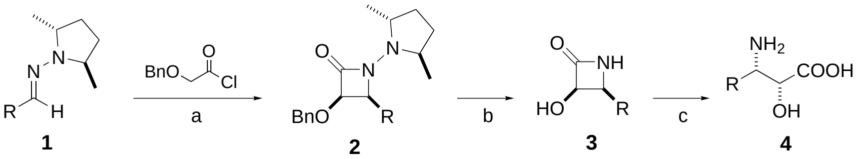
Y. Selzer,* A. Salomon, J. Ghabboun,
D. Cahen* 827–830

Voltage-Driven Changes in Molecular Dipoles Yield Negative Differential Resistance at Room Temperature

Keywords: mercury · molecular devices · monolayers · self-assembly · semiconductors · Umpolung

---

To overcome the limitations of using unstable imines in Staudinger cycloadditions to ketenes, aldehyde *N*,*N*-dialkylhydrazones **1** were used as stable imines. This strategy and a fine tuning of the auxiliary result in a straightforward synthesis of cycloadducts **2**, deprotected *β*-lactams **3**, and isoserines **4** (see scheme: a) Et_3N, toluene, △; b) 1. magnesium monoperoxyphthalate, 2. H_2, Pd/C; c) H^+).



Angew. Chem. **2002**, *114*, 859–861

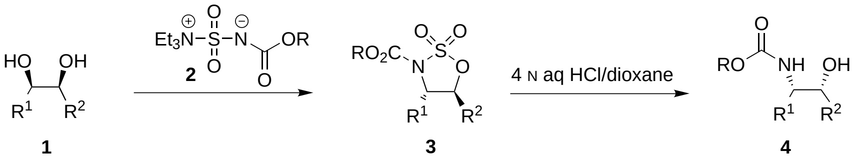
R. Fernández, A. Ferrete,
J. M. Lassaletta,* J. M. Llera,*
E. Martín-Zamora 831–833

N,*N*-Dialkylhydrazones as the Imine Component in the Staudinger-Like [2+2] Cycloaddition to Benzyloxyketene

Keywords: asymmetric synthesis · cycloaddition · hydrazones · lactams · synthetic methods

---

An increasingly targeted functional motif in organic synthesis is the ubiquitous chiral *β*-amino alcohol. A novel two-step approach for the regio- and stereoselective synthesis of a wide variety of 1,2-amino alcohols **4** involves the initial construction of chiral sulfamidates **3** from enantiopure diols **1**, mediated by Burgess reagent (**2**, R = Me), followed by mild treatment with aqueous acid. Furthermore, the development of several new Burgess-type reagents **2** (R = CH_2Ph, CH_2-*o*-NO_2Ph, CH_2CHCH_2, CH_2CCl_3) greatly extends the applications of this protocol.



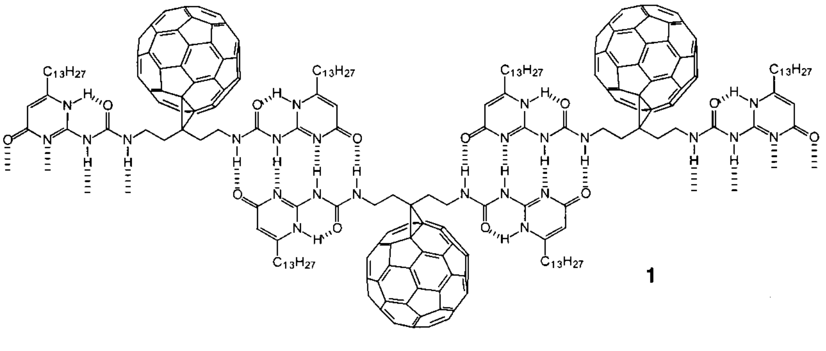
Angew. Chem. **2002**, *114*, 862–866

K. C. Nicolaou,* X. Huang, S. A. Snyder,
P. Bheema Rao, M. Bella,
M. V. Reddy 834–838

A Novel Regio- and Stereoselective Synthesis of Sulfamidates from 1,2-Diols Using Burgess and Related Reagents: A Facile Entry into *β*-Amino Alcohols

Keywords: amino alcohols · asymmetric synthesis · Burgess reagents · sulfamidates · synthetic methods

Bucky balls and chains: The quadruple hydrogen-bonded fullerene array **1** was synthesized and fully characterized. In the highly dynamic polymeric state, the chemical integrity of the monomeric moiety is fully preserved, also with respect to its redox and UV/Vis behavior. Hence, **1** can potentially serve as a building block in supramolecular electronics.



Angew. Chem. **2002**, *114*, 866 – 868

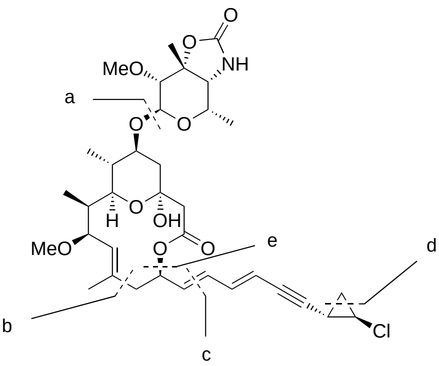
L. Sánchez, M. T. Rispens,
J. C. Hummelen* .... 838 – 840

A Supramolecular Array of Fullerenes by Quadruple Hydrogen Bonding

Keywords: cyclic voltammetry · fullerenes · hydrogen bonds · polymers · supramolecular chemistry

---

A series of highly stereospecific reactions were used in the total synthesis of callipeltoside A (**1**), thus allowing the assignment of its absolute and relative configuration. a) Schmidt glycosylation, b) Ru Alder – ene coupling, c) Emmons – Wadsworth – Horner olefination, d) chiral auxiliary directed alkylation, e) asymmetric allylic Pd alkylation.



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Angew. Chem. **2002**, *114*, 869 – 871

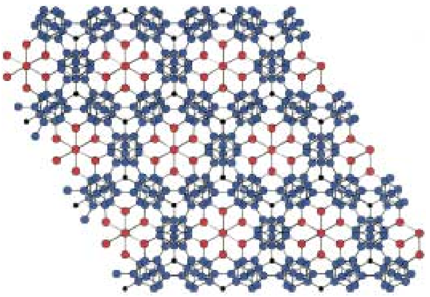
B. M. Trost,* O. Dirat,
J. L. Gunzner .... 841 – 843

Callipeltoside A: Assignment of Absolute and Relative Configuration by Total Synthesis

Keywords: asymmetric synthesis · configuration determination · natural products · total synthesis

---

Synthesis in molten gallium provides access to a new class of boron-rich quaternary phases. Its first member, $Tb_{1.8}C_2Si_8(B_{12})_3$, represents a new structure type in which B_{12} icosahedra, eight Si atoms in a staggered ethane-like arrangement, and C_2 units are interconnected (see picture; red: Si, blue: B, black: C). The Tb sites have a partial occupation of about 60 %.



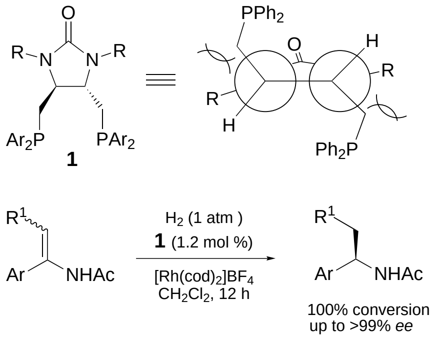
Angew. Chem. **2002**, *114*, 872 – 874

J. R. Salvador, D. Bilc, S. D. Mahanti,
M. G. Kanatzidis* .... 844 – 846

Gallium Flux Synthesis of $Tb_{3-x}C_2Si_8(B_{12})_3$: A Novel Quaternary Boron-Rich Phase Containing B_{12} Icosahedra

Keywords: boron · gallium · high-temperature chemistry · lanthanides · silicon

Appropriate *gauche* steric interactions between the N-substituents and the phosphanylmethyl groups (see picture, top right) in the novel 1,4-diphosphane ligands **1** having an imidazolidin-2-one backbone affect the conformational flexibility of the seven-membered chelate ring formed by coordination to a metal atom. Thus, Rh complexes of **1** are excellent catalysts for enantioselective hydrogenation of enamides (bottom, cod = cyclooacta-1,5-diene).



Angew. Chem. **2002**, *114*, 875 – 877

S.-g. Lee,* Y. J. Zhang, C. E. Song, J. K. Lee, J. H. Choi .... 847 – 849

Novel 1,4-Diphosphanes with Imidazolidin-2-one Backbones as Chiral Ligands: Highly Enantioselective Rh-Catalyzed Hydrogenation of Enamides

Keywords: asymmetric catalysis · hydrogenation · P ligands · rhodium

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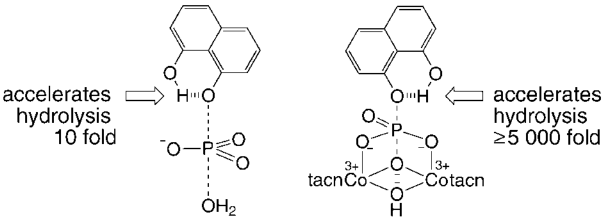
An intramolecular OH group can become much more effective in promoting phosphate hydrolysis when combined with multiple interactions in a model for the metallophosphatase active site (see picture; tacn = 1,4,7-triazacyclononane).



Angew. Chem. **2002**, *114*, 877 – 880

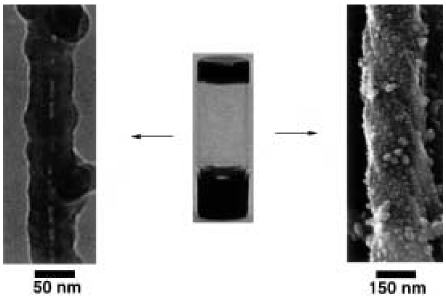
M. Forconi, N. H. Williams* .. 849 – 852

Mimicking Metallophosphatases: Revealing a Role for an OH Group with No Libido

Keywords: cooperative effects · enzyme models · hydrolysis · metalloenzymes

---

Elaborate transcription of unimolecular stacks or helically bundled fibers of sugar-appended porphyrin gelators into silica by sol – gel polycondensation of tetraethoxysilane gives unique hollow silica fibers with a monodispersed 4-nm inner diameter (left picture) and huge helical silica bundles (right picture), respectively.



Angew. Chem. **2002**, *114*, 881 – 884

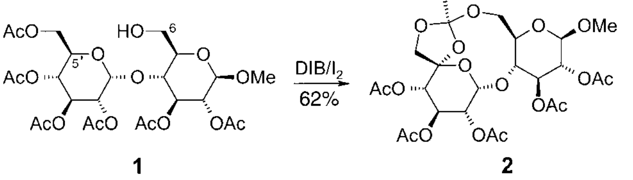
S.-i. Tamaru, M. Takeuchi, M. Sano, S. Shinkai* .... 853 – 856

Sol – Gel Transcription of Sugar-Appended Porphyrin Assemblies into Fibrous Silica: Unimolecular Stacks versus Helical Bundles as Templates

Keywords: organogel · porphyrinoids · self-assembly · silicates · sol – gel processes

---

A nine-membered transition state characterizes the regioselective abstraction of the proton at $C_{5'}$ that leads to the orthoacetate **2** as the product. The alkoxy radical intermediate is obtained from the Glc-α1 $\rightarrow$4-Glc derivative **1** with (diacetoxyiodo)benzene (DIB) and iodine. A similar 1,8-hydrogen abstraction results when the alkoxy radical intermediate is generated under reductive conditions.



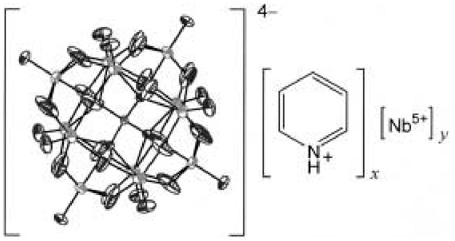
Angew. Chem. **2002**, *114*, 884 – 886

C. G. Francisco, A. J. Herrera, A. R. Kennedy, D. Melián, E. Suárez* .... 856 – 858

Intramolecular 1,8-Hydrogen Abstraction Between Glucopyranose Units in a Disaccharide Model Promoted by Alkoxy Radicals

Keywords: carbohydrates · conformation analysis · glycosides · hydrogen transfer · radical reactions

A niobium and pyridine salt of molybdo(vanado)phosphoric acid (see formula) leads to a catalyst that achieves excellent yield and productivity for both the conversion of propane into acrylic acid and *n*-butane into maleic acid. The catalyst is active under either hydrocarbon-rich or -lean reaction conditions.



Angew. Chem. **2002**, *114*, 886 – 888

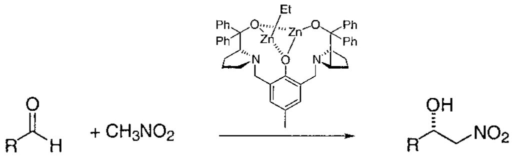
M. E. Davis,* C. J. Dillon, J. H. Holles, J. Labinger .... 858 – 860

A New Catalyst for the Selective Oxidation of Butane and Propane

Keywords: alkanes · carbonyl compounds · heterogeneous catalysis · oxidation · polyoxometalates

---

A high level of enantioselectivity (78 – 93 % *ee*) and high yields (58 – 90 %) are obtained in the enantioselective nitroaldol reaction of nitromethane with several aldehydes when a novel dinuclear zinc catalyst is employed (see scheme).



Angew. Chem. **2002**, *114*, 889 – 891

B. M. Trost,* V. S. C. Yeh ..... 861 – 863

A Dinuclear Zn Catalyst for the Asymmetric Nitroaldol (Henry) Reaction

Keywords: asymmetric catalysis · chiral ligands · nitroaldol reaction · zinc

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

Accelerated publications

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