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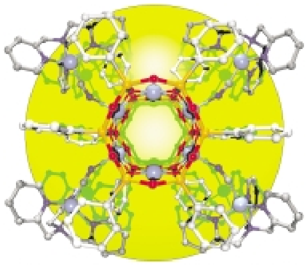
2002
41/23
Pages 4355–4594

COVER PICTURE

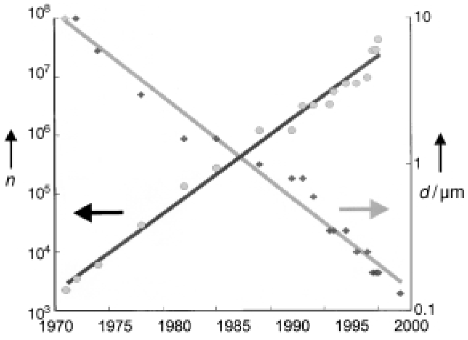


The cover picture shows a magnetic cluster, which was rationally designed by following a two-step synthetic approach (color code: light blue = Cu, orange = Si, gray and white = C, dark blue = N, red = O). The compound, which features ten copper(II) ions in three different coordination environments (trigonal-bipyramidal, square-pyramidal and square-planar), was obtained in crystalline form by self-assembly of four monodentate $[Cu(tmpa)(CN)]^+$ units (tmpa = tris(2-pyridylmethyl)amine) around a preformed hexacopper(II)-siloxanolate cage, $[Cu_6\{(PhSiO_2)_6\}_2]$. Further details on the synthesis, structure, and magnetic properties are reported by G. L. Abbati, A. Cornia et al. on p. 4517 ff.

REVIEWS

Contents

The current state of molecular electronics: Following Moore's law the ultimate miniaturization of electronic devices is molecular-scale electronics (see picture; n = number of transistors per cm^2, d = the pitch size). Although several critical challenges remain unmet, a lot has been learned about how molecules behave in device architectures. This review summarizes what is only the beginning of molecular electronics.

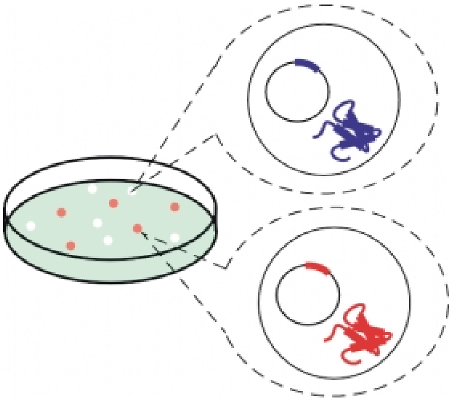


Angew. Chem. **2002**, *114*, 4556–4579

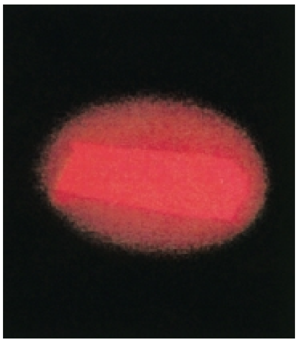
R. L. Carroll,
C. B. Gorman* 4378–4400

The Genesis of Molecular Electronics

Keywords: molecular electronics · molecular switches · monolayers · scanning-probe techniques



MINIREVIEW

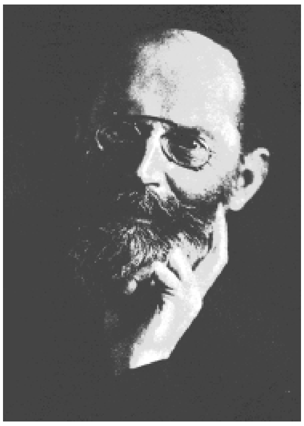


VIPs

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.org

ESSAY

The founder of the chemistry of primary natural products (carbohydrates, purines and nucleosides, and peptides and proteins) was Emil Fischer (see picture). He elucidated the stereochemistry of carbohydrates, introduced the assignment of configuration, developed asymmetric syntheses and protecting-group chemistry, and was the first to obtain synthetic peptides by targeted chain extension. He uncovered the substrate selectivity and stereoselectivity of enzyme reactions, formulated the lock-and-key principle of biological recognition, and became the father of biochemistry. He was born 150 years ago, and 100 years ago he received the Nobel Prize for Chemistry.



Angew. Chem. **2002**, *114*, 4619–4632

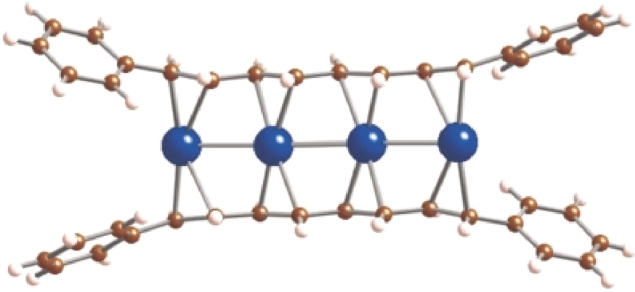
H. Kunz* 4439–4451

Emil Fischer—Unequalled Classicist, Master of Organic Chemistry Research, and Inspired Trailblazer of Biological Chemistry

Keywords: asymmetric synthesis · carbohydrates · Fischer, Emil · history of chemistry

HIGHLIGHT

A new link in the chain: After a long period of inactivity, research into one-dimensional compounds based on linear arrays of transition metals is experiencing a renaissance. Recently, oligomeric and polymeric chains have been reported for a variety of transition metals. One such compound of a particularly exotic variety is depicted here, in which a $\{Pd_4\}^{2+}$ unit is surrounded by a "π-electron sheath" of conjugated polyene ligands.



Angew. Chem. **2002**, *114*, 4633–4637

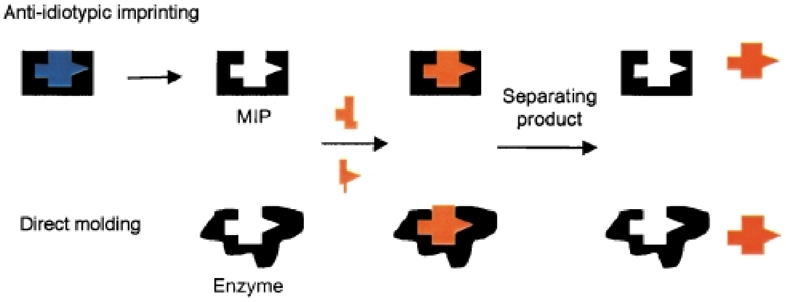
J. K. Bera, K. R. Dunbar* .. 4453–4457

Chain Compounds Based on Transition Metal Backbones: New Life for an Old Topic

Keywords: chain structures · conducting materials · metal–metal interactions · nanotechnology · transition metals

COMMUNICATIONS

Two mutually complementary, target-directed synthetic approaches have been used to generate a class of bio-effective molecules (inhibitors). In the first, condensation reactions were performed within the cavities of a molecularly imprinted polymer (MIP) prepared against a known kallikrein inhibitor. In the second approach, the enzyme itself directed the assembly of small building blocks within the biologically active site (see scheme).



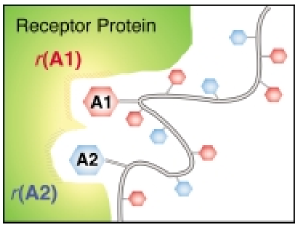
Angew. Chem. **2002**, *114*, 4640–4643

Y. Yu, L. Ye,* K. Haupt,
K. Mosbach* 4459–4463

Formation of a Class of Enzyme Inhibitors (Drugs), Including a Chiral Compound, by Using Imprinted Polymers or Biomolecules as Molecular-Scale Reaction Vessels

Keywords: biomimetic synthesis · drug research · imprinting · inhibitors

A highly practical strategy for mimicking the synthesis of cell-surface oligosaccharides involves the segmentation of a given oligosaccharide into polymerizable carbohydrate modules containing two glycoside residues (A1 and A2) that provide key binding interactions with the receptor protein at the *r*(A1) and *r*(A2) binding sites. The bioactive structures are then regenerated by radical copolymerization.



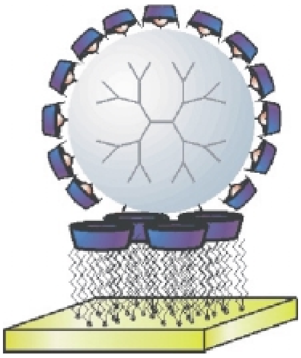
K. Sasaki, Y. Nishida,* T. Tsurumi, H. Uzawa, H. Kondo, K. Kobayashi* . . . . 4463 – 4467

Facile Assembly of Cell Surface Oligosaccharide Mimics by Copolymerization of Carbohydrate Modules

Keywords: biomimetic synthesis · carbohydrates · oligosaccharides · polymers · sialic acids

Angew. Chem. **2002**, *114*, 4643 – 4647

Monolayers of cyclodextrin host molecules on gold substrates are used as “molecular printboards” for the stable attachment of functionalized molecules through multiple supramolecular interactions. Adsorption is achieved through delivery as a supramolecular complex (see picture), whereas the desorption kinetics can be tuned by varying the cyclodextrin concentration in solution.



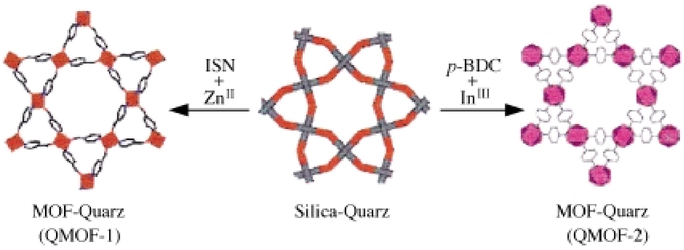
J. Huskens,* M. A. Deij, D. N. Reinhoudt* . . . . 4467 – 4471

Attachment of Molecules at a Molecular Printboard by Multiple Host – Guest Interactions

Keywords: cyclodextrins · host – guest systems · monolayers · self-assembly · surface plasmon resonance

Angew. Chem. **2002**, *114*, 4647 – 4651

Man-made minerals: The synthesis of two α- and β-quartz structures with open metal – organic frameworks (QMOF-1 and QMOF-2) is reported. QMOF-1 is assigned to $Zn(ISN)_2 \cdot 2H_2O$ (ISN = isonicotinic acid) with the low symmetry of α-quartz, while QMOF-2 to $InH(BDC)_2$ (BDC = terephthalate) with the high symmetry of β-quartz.



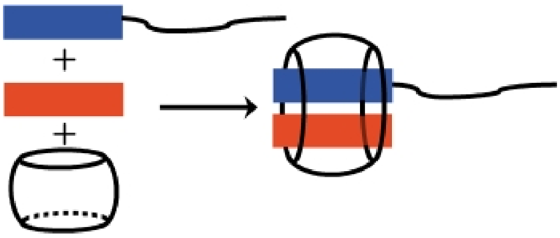
J. Sun, L. Weng, Y. Zhou, J. Chen, Z. Chen, Z. Liu, D. Zhao* . . 4471 – 4473

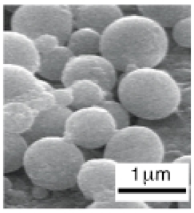
QMOF-1 and QMOF-2: Three-Dimensional Metal – Organic Open Frameworks with a Quartzlike Topology

Keywords: carboxylate ligands · chirality · coordination polymers · microporus materials · supramolecular chemistry · zeolite analogues

Angew. Chem. **2002**, *114*, 4651 – 4653

A stable ternary inclusion complex comprising a host, an electron donor, and an electron acceptor with a long alkyl tail (see schematic representation) triggers the spontaneous formation of giant vesicles (see TEM image). The ternary complex behaves as a supramolecular amphiphile with a large polar head group and a single hydrophobic tail. Treatment of the complex with an oxidizing agent results in disruption of the vesicles.





Y. J. Jeon, P. K. Bharadwaj, S. Choi, J. W. Lee, K. Kim* . . . . 4474 – 4476

Supramolecular Amphiphiles: Spontaneous Formation of Vesicles Triggered by Formation of a Charge-Transfer Complex in a Host

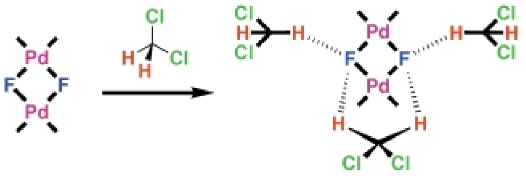
Keywords: charge transfer · cucurbituril · host – guest systems · supramolecular chemistry · vesicles

Angew. Chem. **2002**, *114*, 4654 – 4656

V. V. Grushin,*
W. J. Marshall 4476–4479

Is Fluoride Bonded to Two Pd Acceptors Still Basic? Three CH_2Cl_2 Molecules Encapsulating a $Pd_2(\mu\text{-}F)_2$ Square and New Implications for Catalysis

The unexpectedly high basicity of bridging fluoride ions in novel dinuclear Pd complexes is manifested by intramolecular CH⋯F interactions and the unprecedented hydrogen bonding of three CH_2Cl_2 molecules to the Pd_2F_2 framework (see scheme). Novel deprotonation of a coordinated $(alkyl)_3P$ ligand to produce a bifluoride is reported.



Angew. Chem. **2002**, *114*, 4656–4659

Keywords: fluorides · hydrogen bonds · palladium · X-ray diffraction

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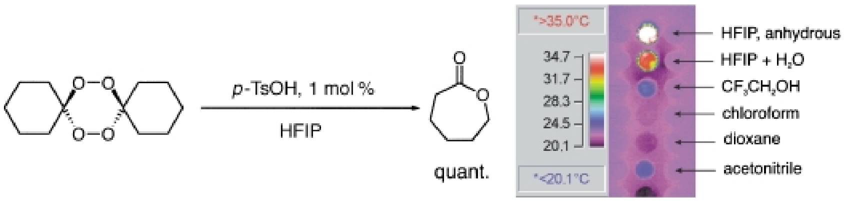
A. Berkessel,* M. R. M. Andreae,
H. Schmickler, J. Lex 4481–4484

Baeyer–Villiger Oxidations with Hydrogen Peroxide in Fluorinated Alcohols: Lactone Formation by a Nonclassical Mechanism

What a difference the solvent makes! Unlike in conventional solvents, non-strained ketones such as cyclohexanone react smoothly with hydrogen peroxide in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) to give lactones. The reaction proceeds via an isolatable spiro-bisperoxide, which undergoes a highly exothermic acid-catalyzed rearrangement to two equivalents of lactone (see Equation and IR thermogram).



Angew. Chem. **2002**, *114*, 4661–4664

Keywords: Baeyer–Villiger oxidation · fluorinated solvents · IR thermography · peroxides · rearrangement

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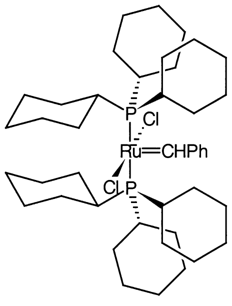
C. Adlhart, P. Chen* 4484–4487

Ligand Rotation Distinguishes First- and Second-Generation Ruthenium Metathesis Catalysts

QM/MM provides a new twist: In olefin metathesis with first-generation Ru catalyst **1**, the rotation of the phosphane ligand with threefold symmetry is the rate-determining step. Second-generation catalyst **2** is more active: the rotation step is not required as the carbene ligand has twofold symmetry. Combined QM/MM calculations confirm the results of earlier experimental investigations.



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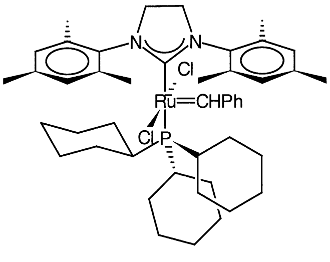

2

Angew. Chem. **2002**, *114*, 4668–4671

Keywords: density-functional calculations · force-field calculations · homogeneous catalysis · metathesis · theoretical chemistry

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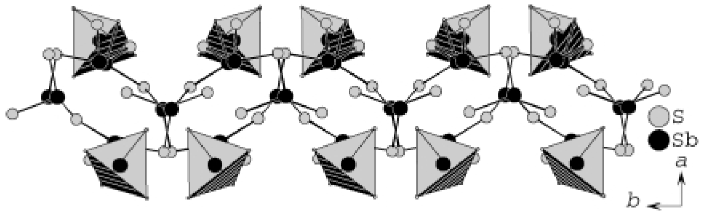
R. Stähler, B.-D. Mosel, H. Eckert,
W. Bensch* 4487–4489

Solvothermal Synthesis, Crystal Structure, Thermal Stability, and Mössbauer Spectroscopic Investigation of the Mixed-Valent Thioantimonate(III,V) $[Ni(dien)_2]_2Sb_4S_9$

Antimony in two oxidation states: The mixed-valent thioantimonate anion $[Sb_4S_9]^{4-}$ in the compound $[Ni(dien)_2]_2Sb_4S_9$ contains Sb^VS_4 tetrahedra, which are bound by one terminal S atom to the Sb_3S_7 backbone of the anion (see figure). dien = diethylenetriamine.

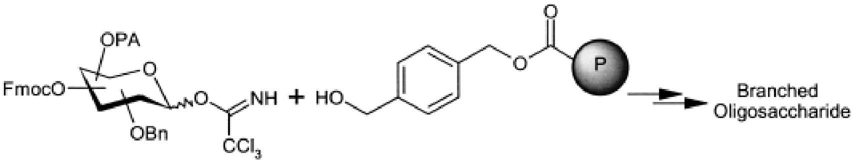


Angew. Chem. **2002**, *114*, 4671–4673

Keywords: antimony · mixed-valent compounds · Moessbauer spectroscopy · solvothermal synthesis · structure elucidation

1433-7851/02/4123-4361 $ 20.00+.50/0

A solid basis for sugar synthesis: A simple, yet efficient method for the regio- and stereocontrolled synthesis of linear and branched oligosaccharides on a solid support should be an important step forward for the development of generally applicable automated oligosaccharide syntheses. The combination of different esters (9-fluorenylmethyloxycarbonyl (Fmoc), phenoxyacetate (PA), benzoyl) for temporary, or *O*-benzyl groups for permanent protection as well as binding to the solid phase and *O*-glycosyl trichloroacetimidates as donors offers this possibility, as shown in the synthesis of an *N*-glycan hexasaccharide (see scheme).



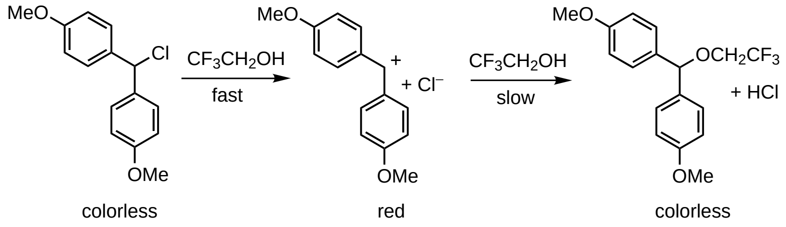
Angew. Chem. **2002**, *114*, 4664–4668

X. Wu, M. Grathwohl,
R. R. Schmidt* 4489–4493

Efficient Solid-Phase Synthesis of a Complex, Branched *N*-Glycan Hexasaccharide: Use of a Novel Linker and Temporary-Protecting-Group Pattern

Keywords: glycosidation • *N*-glycans • oligosaccharides • protecting groups • solid-phase synthesis

Which step is faster? Carbocations are not necessarily short-lived intermediates in solvolytic displacement reactions. In many cases, ionization of the carbocation's precursor is faster than the subsequent reaction with the solvent (see scheme), which allows one to directly observe the intermediate carbocation.



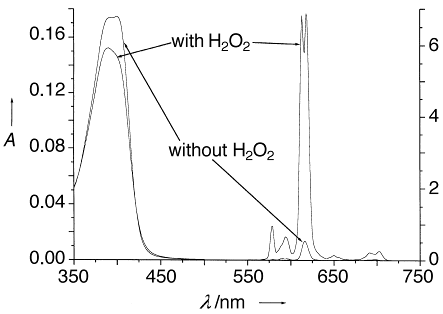
Angew. Chem. **2002**, *114*, 4674–4676

H. Mayr,* S. Minegishi 4493–4495

First Direct Observation of the Two Distinct Steps in an S_N1 Reaction

Keywords: carbocations • nucleophilic substitution • reaction kinetics • reactive intermediates • solvent effects • solvolysis

A bright idea: A 15-fold increase in fluorescence intensity occurs when the complex formed between Eu^{3+} and the antibiotic tetracycline binds to hydrogen peroxide at neutral pH. The complex can be used in the determination of the concentration of H_2O_2, the activity of oxidases, the concentration of glucose, and also in an optical sensor for H_2O_2.



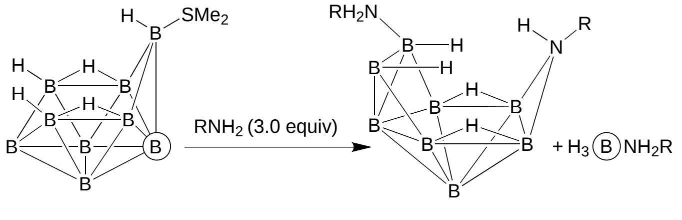
Angew. Chem. **2002**, *114*, 4681–4684

O. S. Wolfbeis,* A. Dürkop, M. Wu,
Z. Lin 4495–4498

A Europium-Ion-Based Luminescent Sensing Probe for Hydrogen Peroxide

Keywords: fluorescent probes • hydrogen peroxide • lanthanides • oxidases • sensors

The great escape! In the transition of $(Me_2S)B_9H_{13}$ into $(RH_2N)B_8H_{11}NHR$, one boron atom is lost. Boron-substituted derivatives of $(Me_2S)B_9H_{13}$ were used to identify this boron atom, which turned out to be firmly integrated in the starting cluster (see scheme). A pathway for the conversion is proposed.



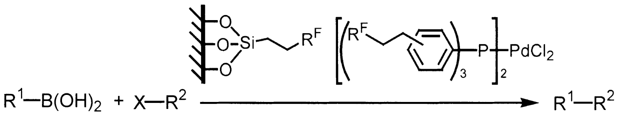
Angew. Chem. **2002**, *114*, 4676–4678

M. E. El-Zaria,* U. Dörfler,
M. Hofmann, D. Gabel 4498–4500

Conversion of *arachno*-Nonaborane into Azanonaborane: Unexpected Loss of a Firmly Integrated Boron Atom

Keywords: boranes • boron • cluster compounds • NMR spectroscopy • rearrangements

With and now without: Perfluoro-tagged catalysts immobilized on fluorous reversed-phase silica gel can be used for Suzuki and Sonogashira C–C coupling reactions (see scheme; R^1 = e.g., phenyl, 4-$MeOC_6H_4$, R^2 = e.g., 4-$NO_2C_6H_4$, 4-$MeCOC_6H_4$, X = Br, I) without the need for perfluorinated solvents. After the reaction the products were isolated by decantation and the Pd catalysts were recovered and reused.



Angew. Chem. **2002**, *114*, 4678–4681

C. C. Tzschucke, C. Markert, H. Glatz, W. Bannwarth* 4500–4503

Fluorous Biphasic Catalysis without Perfluorinated Solvents: Application to Pd-Mediated Suzuki and Sonogashira Couplings

Keywords: biaryls • C–C coupling • fluorous biphasic catalysis • supported catalysts

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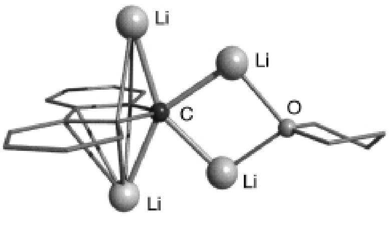
Six-coordinate carbon: 9,9-Dilithiofluorene–thf complex (see picture) crystallizes as chains of lithium atoms which are alternately bridged by fluorenylidene and THF units. These polymer chains are held together by Li–C π and σ interactions; the tetrametallated carbon atom is six-coordinated. This means, structural elements are found here, which are known from lithioalkanes, on the one hand, and from the lithocene anion, on the other hand.



Angew. Chem. **2002**, *114*, 4685–4687

G. Linti,* A. Rodig, H. Pritzkow 4503–4506

9,9-Dilithiofluorene: The First Crystal-Structure Analysis of an α,α-Dilithiated Hydrocarbon

Keywords: carbanions • density functional calculations • lithiation • lithium • structure determination

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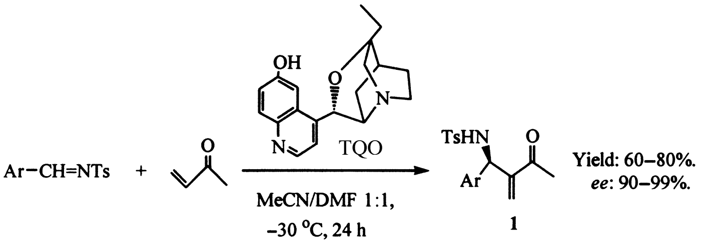
The chiral Lewis base catalyst TQO, a cinchona alkaloid derivative, facilitates the Baylis–Hillman reaction of various *N*-arylidene-4-methylbenzenesulfonamides with methyl vinyl ketone (MVK) or methyl acrylate to give the Baylis–Hillman adducts **1** in good yields with high enantioselectivity (90–99% *ee*).



Angew. Chem. **2002**, *114*, 4689–4692

M. Shi,* Y.-M. Xu 4507–4510

Catalytic, Asymmetric Baylis–Hillman Reaction of Imines with Methyl Vinyl Ketone and Methyl Acrylate

Keywords: asymmetric catalysis • asymmetric synthesis • Baylis–Hillman reactions • C–C coupling • Lewis bases

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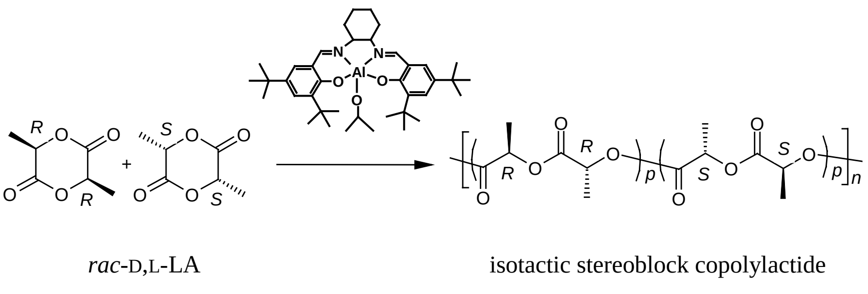
Easily accessible [(salen)(*i*PrO)Al] exerts excellent molecular-weight and stereochemical control in lactide polymerization either in solution or in the absence of solvent. The *R,R* initiator shows a marked preference for L-lactide over D-lactide. Stereoblock copolylactides (see scheme) with high melting points can be prepared directly from D,L-lactides by using a racemic initiator.



rac-D,L-LA

isotactic stereoblock copolylactide

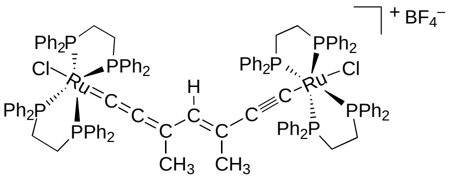
Angew. Chem. **2002**, *114*, 4692–4695

Z. Zhong, P. J. Dijkstra, J. Feijen* 4510–4513

[(salen)Al]-Mediated, Controlled and Stereoselective Ring-Opening Polymerization of Lactide in Solution and without Solvent: Synthesis of Highly Isotactic Polylactide Stereocopolymers from Racemic D,L-Lactide

Keywords: aluminum • polymers • ring-opening polymerization • stereoselectivity

A planar "W"-shaped π-conjugated C_7 bridge occurs in the bimetallic complexes, such as **1**, that are formed by addition of cationic ruthenium allenylidenes to the $C_\gamma \equiv C_\delta$ bond of a ruthenium diyne. These complexes possess attractive redox and optical properties that can be tuned by varying the pendant groups.



1

Angew. Chem. **2002**, *114*, 4695–4699

S. Rigaut, J. Massue, D. Touchard,*
J.-L. Fillaut, S. Golhen,
P. H. Dixneuf 4513–4517

Unprecedented Coupling of Allenylidene and Diynyl Metal Complexes: A Bimetallic Ruthenium System with a C_7 Conjugated Bridge

Keywords: allenylidenes · bimetallic complexes · bridging ligands · cumulenes · ruthenium

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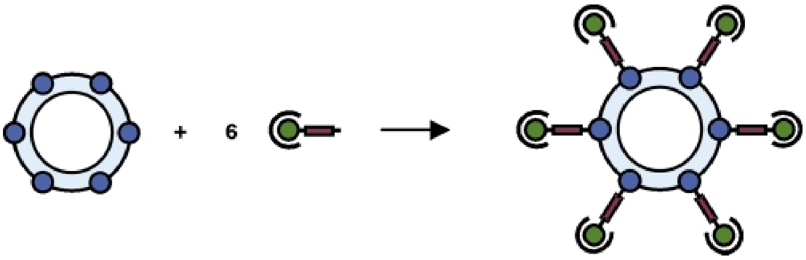
A decacopper(II) cluster. Clusters (shown in blue) can be expanded and their magnetic properties tuned by the addition of suitable metal-complex ligands (shown in green). By using this method, $[Cu_6\{(PhSiO_2)_6\}_2\{(NC)Cu(tmpa)\}_4](PF_6)_4$ was rationally designed by self-assembly of four $\{(NC)Cu(tmpa)\}^+$ units around a robust hexacopper(II)-siloxanolate cage (tmpa = tris(2-pyridylmethyl)amine).



Angew. Chem. **2002**, *114*, 4699–4702

G. L. Abbati,* A. Caneschi, A. Cornia,*
A. C. Fabretti, Y. A. Pozdniakova,
O. I. Shchegolikhina 4517–4520

Towards Stepwise Cluster Assembly: A Decacopper(II) Complex Obtained by Controlled Expansion of a Metallasiloxane Cage

Keywords: cluster compounds · copper · cyanides · magnetic properties · synthesis design

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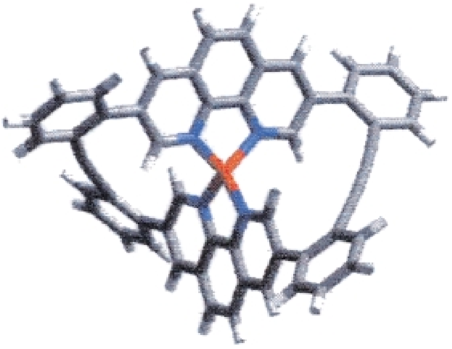
A helical home for copper: A sequential, in situ desilylation/dimerization/decomplexation protocol has been used to generate helical enyne-bridged heterocycles in a copper(I) templated synthesis. Variable temperature ^{13}C NMR analysis of the copper complex (see calculated structure) indicated the barrier to helical isomerization was 13.6 kcal mol^{-1}, an increase of about 4 kcal mol^{-1} relative to the uncomplexed cyclophane.



Angew. Chem. **2002**, *114*, 4702–4705

M. A. Heuft, A. G. Fallis* .. 4520–4523

Template-Directed Synthesis of Helical Phenanthroline Cyclophanes

Keywords: copper · cyclophanes · helical structures · N ligands · template synthesis

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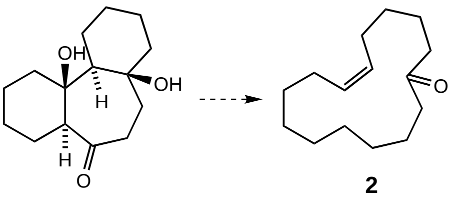
The scent of success! New highly valued unsaturated C-15-macrocyclic musks were synthesized in a stereocontrolled manner by two consecutive fragmentations, starting from tricyclic dihydroxy ketone **1**.



1 **2**

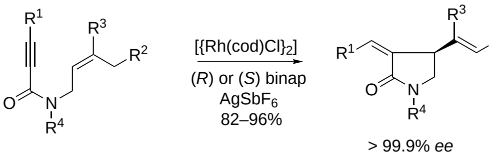
Angew. Chem. **2002**, *114*, 4705–4708

C. Fehr,* J. Galindo, O. Etter,
W. Thommen 4523–4526

Access to C-15 Macrocyclic Ketones by Iterative Fragmentations of a Tricyclic System

Keywords: fragmentation · fragrances · ketones · macrocycles · reduction

Values of over 99 % *ee* were obtained for all the tested substrates in the Rh^I-catalyzed Alder-ene reaction, as applied to the highly enantioselective formation of functionalized lactams. In most cases, α-substituted γ-butyrolactams were obtained in high yields by simply mixing commercially available [{Rh(cod)Cl}$_2$] and binap with the substrates (see scheme).



R^1 = aryl, alkyl, alkoxy
R^2 = alkyl, acetoxy, alkoxy, amide
R^3 = H, Me
R^4 = Bn, Me, Ts

Angew. Chem. **2002**, *114*, 4708 – 4711

A. Lei, J. P. Waldkirch, M. He,
X. Zhang* .... 4526 – 4529

Highly Enantioselective Cycloisomerization of Enynes Catalyzed by Rhodium for the Preparation of Functionalized Lactams

Keywords: enantioselectivity · heterocycles · homogeneous catalysis · rhodium · synthetic methods

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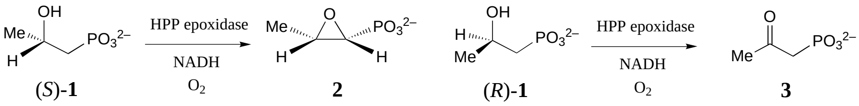
The regiospecificity of the initial H-atom abstraction may explain the fact that HPP epoxidase, a non-heme iron-containing enzyme, catalyzes not only the conversion of (*S*)-HPP ((*S*)-**1**) to fosfomycin (**2**), but also the oxidation of the 1*R* enantiomer, which leads exclusively to **3** with nearly equal efficiency.



Angew. Chem. **2002**, *114*, 4711 – 4714

Z. Zhao, P. Liu, K. Murakami,
T. Kuzuyama, H. Seto,
H.-w. Liu* .... 4529 – 4532

Mechanistic Studies of HPP Epoxidase: Configuration of the Substrate Governs Its Enzymatic Fate

Keywords: biosynthesis · enzymes · fosfomycin · radicals · reaction mechanisms

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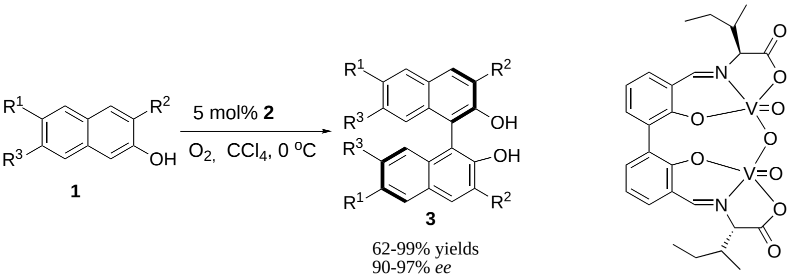
Chiral binaphthols 3 were obtained by oxidative coupling of 2-naphthols in the presence of achiral biphenol-derived diastereomeric V^{IV} oxo complexes. Despite its conformationally flexible biphenyl moiety, the best catalyst **2** (90 – 97 % *ee*, 62 – 99 % yield) exhibits comparable or even higher enantioselectvities than an analogue with an optically pure 1,1′-binaphthyl group.



62-99% yields
90-97% *ee*

2

Angew. Chem. **2002**, *114*, 4714 – 4717

Z. Luo, Q. Liu, L. Gong,* X. Cui, A. Mi,
Y. Jiang .... 4532 – 4535

Novel Achiral Biphenol-Derived Diastereomeric Oxovanadium(IV) Complexes for Highly Enantioselective Oxidative Coupling of 2-Naphthols

Keywords: asymmetric catalysis · binaphthols · C–C coupling · N,O ligands · vanadium

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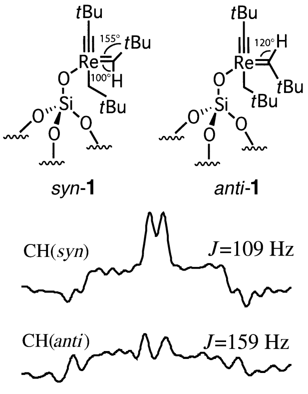
Carbenic $J_{C,H}$ coupling as an indicator of agostic interactions in surface species: In the highly active heterogeneous catalyst for olefin metathesis **1**, this coupling constant is 109 Hz for the *syn* and 159 Hz for the *anti* rotamer. From this, a H-agostic interaction in the *syn* rotamer can be deduced and the high electrophilicity of the Re center can be rationalized.



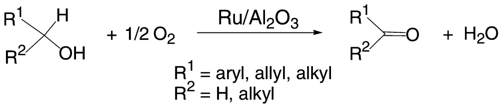
Angew. Chem. **2002**, *114*, 4717 – 4720

A. Lesage, L. Emsley,* M. Chabanas,
C. Copéret,* J.-M. Basset* .. 4535 – 4538

Observation of a H-Agostic Bond in a Highly Active Rhenium – Alkylidene Olefin Metathesis Heterogeneous Catalyst by Two-Dimensional Solid-State NMR Spectroscopy

Keywords: agostic interactions · heterogeneous catalysis · NMR spectroscopy · rhenium

Round and round it goes! A supported ruthenium catalyst, easily prepared by treatment of $RuCl_3$ with γ-Al_2O_3, is an efficient heterogeneous catalyst for the oxidations of alcohols with 1 atm of molecular oxygen or air without any additives (see scheme). The spent catalyst was recyclable without an appreciable loss of the catalytic activity and selectivity for the oxidation.



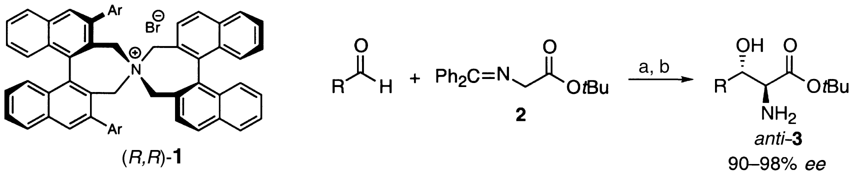
Angew. Chem. **2002**, *114*, 4720–4724

K. Yamaguchi, N. Mizuno* 4538–4542

Supported Ruthenium Catalyst for the Heterogeneous Oxidation of Alcohols with Molecular Oxygen

Keywords: alcohols · heterogeneous catalysis · oxidation · ruthenium · supported catalysts

A practical and environmentally benign chemical process for the synthesis of optically active β-hydroxy-α-amino acids involves the reaction of an aldehyde, glycine Schiff base **2**, in the presence of catalytic *N*-spiro chiral quaternary ammonium bromide **1**. The cross-aldol product **3** is obtained with excellent stereochemical control (see scheme; a) (*R*,*R*)-**1** (2 mol%), toluene/aqueous NaOH (1%), 0° C, 2 h; b) HCl (1N)/THF).



Angew. Chem. **2002**, *114*, 4724–4726

T. Ooi, M. Taniguchi, M. Kameda, K. Maruoka* 4542–4544

Direct Asymmetric Aldol Reactions of Glycine Schiff Base with Aldehydes Catalyzed by Chiral Quaternary Ammonium Salts

Keywords: aldol reactions · amino acids · asymmetric synthesis · phase-transfer catalysis · Schiff bases

Stereochemistry revisited: Density functional theoretical predictions of specific rotation values for (*S*)-bromochlorofluoromethane were obtained using three large basis sets at different wavelengths and compared to the corresponding experimental values. Density functional theoretical predictions of Raman optical activity (ROA) parameters for (*S*)-bromochlorofluoromethane were also obtained and compared to the corresponding experimental values. These data suggest that the absolute configuration of bromochlorofluoromethane is (*S*)-(+).

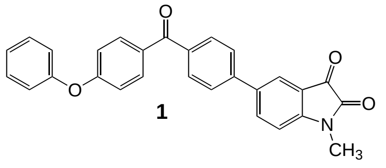
Angew. Chem. **2002**, *114*, 4726–4728

P. L. Polavarapu* 4544–4546

The Absolute Configuration of Bromochlorofluoromethane

Keywords: alkyl halogenides · chirality · density functional calculations · Raman spectroscopy · specific rotation

Excellent thermal stability and a relatively high glass-transition temperature are exhibited by the hyperbranched poly(arylene oxindoles), which were prepared by an acid-catalyzed polycondensation of the substituted isatine **1**. The polymers thus obtained can also be readily functionalized further.



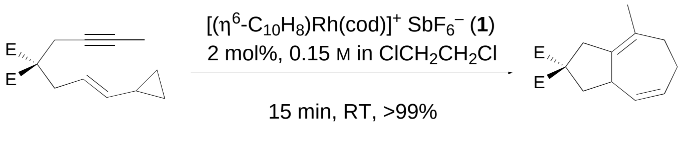
Angew. Chem. **2002**, *114*, 4729–4732

M. Smet,* E. Schacht, W. Dehaen 4547–4550

Synthesis, Characterization, and Modification of Hyperbranched Poly(arylene oxindoles) with a Degree of Branching of 100%

Keywords: dendrimers · isatin · polymerization · polymers · spiro compounds

Within a few minutes at room temperature, intramolecular [5+2] cycloaddition reactions of vinylcyclopropanes and tethered alkenes or alkynes reach completion when arene-ligated rhodium(I) complexes are used as catalysts (see scheme). In particular, naphthalene complex **1** was found to be an exceptionally effective and, in cases where comparisons have been made, preferred catalyst.



Angew. Chem. **2002**, *114*, 4732–4735

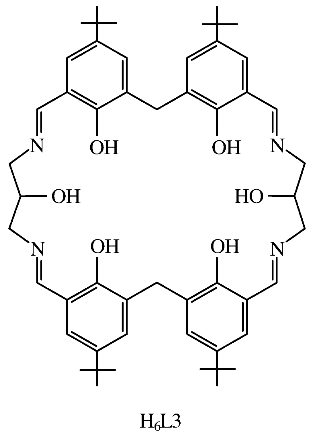
P. A. Wender,* T. J. Williams 4550–4553

$[(arene)Rh(cod)]^+$ Complexes as Catalysts for [5+2] Cycloaddition Reactions

Keywords: arene ligands · cycloaddition · homogeneous catalysis · medium-sized rings · rhodium

The wide range of nuclearity, geometry, and protonation levels possible with the hybrid Schiff base/calixarene ligand H_6L3 are illustrated in the formation and characterization of three different copper(II) complexes. The X-ray structures show the complexes to have clearly defined clefts where exogenous ligands are bound.

Angew. Chem. **2002**, *114*, 4735–4738



H_6L3

J. Barreira Fontecha, S. Goetz,
V. McKee* 4553–4556

Di-, Tri-, and Tetracopper(II) Complexes of a Pseudocalixarene Macrocycle

Keywords: coordination modes · copper · macrocyclic ligands · O ligands · structure elucidation

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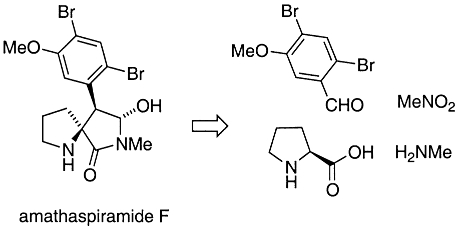
Breaking the *cis* rule: L-Proline and not as expected D-proline led to (−)-amathaspiramide F with the correct configuration in a short sequence of steps (see retrosynthetic scheme). This synthesis features an exception to the principle of self-regeneration of chirality and a strategy for circumventing a problematic Nef reaction in the presence of densely spaced polar functionality.

Angew. Chem. **2002**, *114*, 4738–4741



C. C. Hughes, D. Trauner* .. 4556–4559

The Total Synthesis of (−)-Amathaspiramide F

Keywords: alkaloids · amathaspiramides · Nef reaction · proline · total synthesis

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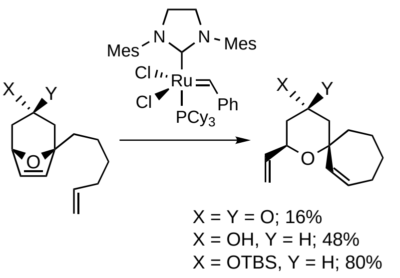
Consecutive ring-opening/ring-closing metathesis reactions of oxabicyclo[3.2.1]octene systems that bear an olefinic tether at the bridgehead lead to highly functionalized, spiroannulated pyrans (see scheme). The facility of the reaction is greatly influenced by remote substituents.

Angew. Chem. **2002**, *114*, 4742–4744



L. C. Usher, M. Estrella-Jimenez,
I. Ghiviriga, D. L. Wright* .. 4560–4562

Synthesis of Functionalized Pyrans by Domino Metathesis Reaction of Oxabicyclo Derivatives: Dramatic Effect of Remote Substituents on Reactivity and Selectivity

Keywords: cyclization · heterocycles · metathesis · pyrans · ruthenium

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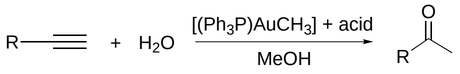
As good as gold: Hydration of alkynes by using gold–acid catalyst systems with high turnover frequencies provides a greener synthetic route to carbonyl compounds in high yields, as shown.

Angew. Chem. **2002**, *114*, 4745–4747

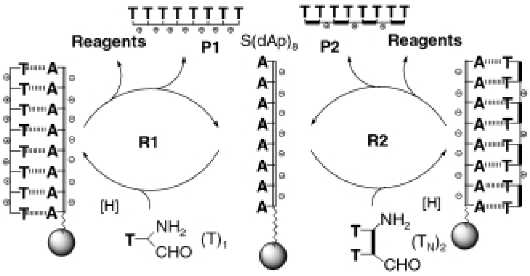


E. Mizushima, K. Sato, T. Hayashi,*
M. Tanaka* 4563–4565

Highly Efficient Au^I-Catalyzed Hydration of Alkynes

Keywords: alkynes · gold · homogeneous catalysis · hydration

A powerful strategy to translate DNA directly into synthetic polymers: A solid-phase synthetic strategy is applied to DNA-templated synthesis by using immobilized native DNA octamer S(dA$_p$)$_8$ as a template to direct the specific polymerization of synthetic DNA analogues (T)$_1$ and (T$_N$)$_2$ (see figure). The solid-supported template provides advantages in chemical amplification and purification.



Angew. Chem. **2002**, *114*, 4749 – 4751

Keywords: DNA replication · polymerization · reduction · solid-phase synthesis · template synthesis

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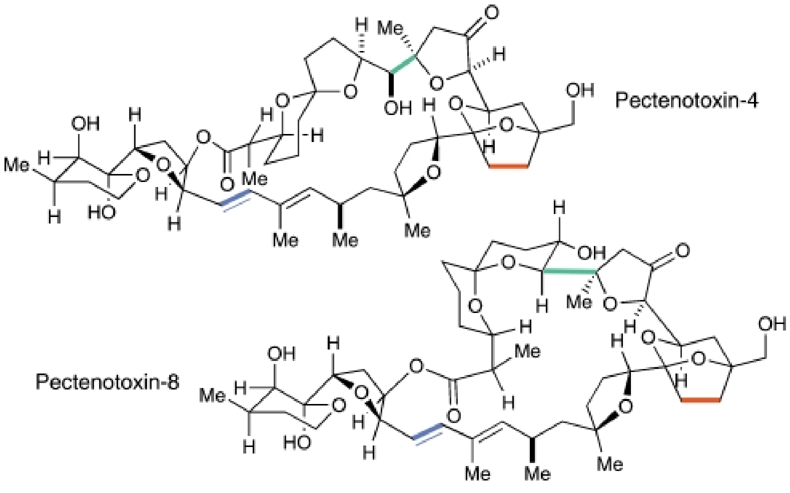
The total syntheses of the marine macrolides pectenotoxins-4 and -8 have been realized. The pectenotoxins are a new class of marine macrolides that exhibit a high level of biological activity. Key fragment couplings include a Felkin-selective Grignard addition reaction (green), a metalated dimethylhydrazone alkylation (red), and a late-stage olefination reaction with a β-alkoxy sulfone (blue). The utility of the *N*-phenylamide as a carboxy surrogate and the use of the base labile *tert*-butoxydiphenylsilyl ether is also described.



Angew. Chem. **2002**, *114*, 4751 – 4755

Keywords: aldol reactions · natural products · pectenotoxin · total synthesis

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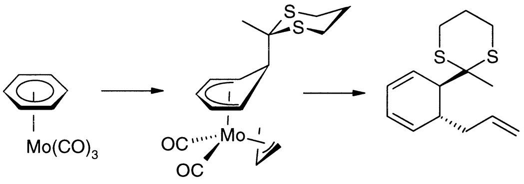
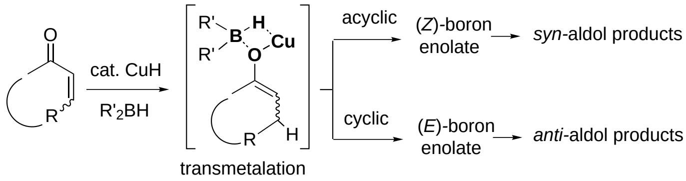
No CO insertion occurs in the first Mo(CO)$_3$-mediated dearomatization reaction sequence (shown). In contrast to the analogous Cr(CO)$_3$ reaction, the intermediate allyl complex can be isolated.



Angew. Chem. **2002**, *114*, 4759 – 4761

Keywords: allylation · arene ligands · molybdenum · nucleophilic addition

Looking for an alternative to prepare your regio- and stereodefined boron enolates? Concerned about using expensive and moisture-sensitive Bu_2BOTf? Consider this new procedure for regiospecific enolization based on a catalytic CuH-initiated 1,4-reduction followed by in situ transmetalation with a simple borane (R'_2BH; see scheme).



Angew. Chem. **2002**, *114*, 4762 – 4764

B. H. Lipshutz,* P. Papa ..... 4580 – 4582

Copper-Catalyzed Reductive Alkylations of Enones: A Novel Transmetalation Protocol

Keywords: boron · copper · hydrides · reduction · transmetalation

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

Accelerated publications

* Author to whom correspondence should be addressed

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Issue 22, 2002 was published online on November 12.

Don't forget all the Tables of Contents from 1998 onwards may be still found on the WWW under: http://www.angewandte.org

In the Communication by **C. Ortiz Mellet**, **J. M. García Fernández et al.** in Issue 19, **2002**, 3674–3676, the addresses of the authors were inadvertently swapped. The new fax number for Dr. Ortiz Mellet is (+34) 95-462-49-60. On page 3675, the sentence starting on line 9 of the first column should read: "Preliminary modeling studies suggested that the inner wall in these macrocycles (cyclotrehalins, CTs)[6] would expose the H-1, H-2, and H-4 protons for contacts with an included guest, ..." On page 3676, line 8 of the second paragraph (first column), "more stable than that with AC" should read "more stable than that with benzoate". In the literature section, references [6] and [8] should be swapped.

In the Communication by **B. Hedman**, **K. O. Hodgson**, **A. Llobet**, **T. D. P. Stack et al.** in Issue 16, **2002**, 2991–2994, Figure 2 and its legendare not correct. The corrected Figure and legend are shown below.

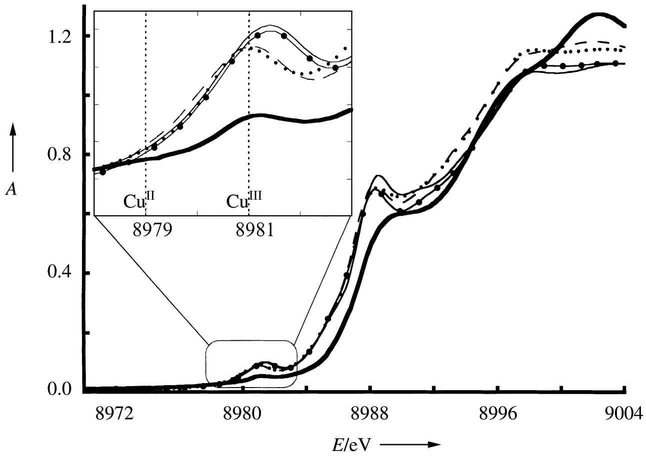
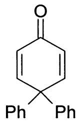


Figure 2. Cu K-edges for Cu^{III} complexes **1**-$(CF_3SO_3)_2$ (——), **1**-$(ClO_4)_2$ (•–•–), **2**-$(ClO_4)_2$ (– – –), **3**-$(ClO_4)_2$ (••••), and $[Cu^{III}(H_{-3}Aib_3)]$[14] (**——**). The amplified inset shows the pre-edge region ($1s \rightarrow 3d_{x^2-y^2}$ transition, 8978–8983 eV). A = normalized absorption, E = energy.

In the Communication by **A. Nangia**, **W. T. Robinson**, **J. A. K. Howard**, **F. H. Allen et al**. in Issue 20, **2002**, 3848–3851, the structural formula of diphenylcyclohexadienone **1** on page 3848 was inadvertently cut off on the right-hand side. The correct formula is shown below.



1