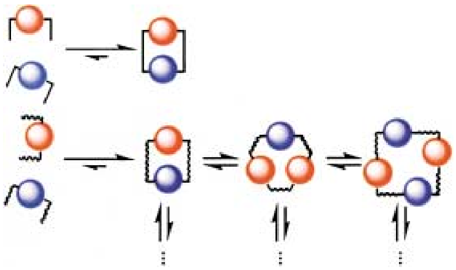
# COVER PICTURE

**The cover picture shows** the electric eel, *Electrophorus electricus*, a source for commercially available acetylcholinesterase. In an experiment described by K. B. Sharpless and M. G. Finn and co-workers on pp. 1053–1057, a femtomolar inhibitor was assembled by the enzyme from a collection of building blocks containing azide and alkyne functional groups, shown floating in solution. The templated 1,3-dipolar cycloaddition reaction, producing the inhibitor, is represented by the flare of light at the center of the image.

# REVIEW

**Supramolecular chemistry at the covalent level!** That is the mouth-watering prospect that dynamic covalent chemistry offers the chemist. Covalent synthesis under thermodynamic control can either result in the self-assembly of a single molecular architecture (see scheme, top), if the monomer is rigid and correctly predisposed, or the formation of adaptable libraries (bottom), if the monomer contains some flexibility programmed into it.



*Angew. Chem.* **2002**, *114*, 938–993

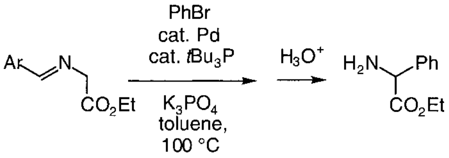
S. J. Rowan,* S. J. Cantrill,
G. R. L. Cousins, J. K. M. Sanders,
J. F. Stoddart ................. 898–952

Dynamic Covalent Chemistry

**Keywords:** catenanes · combinatorial libraries · macrocycles · polymers · rotaxanes · supramolecular chemistry

# HIGHLIGHTS

**Fine tuning for fine chemicals**: Two complimentary and yet intimately related methods for the palladium-catalyzed arylation of esters and their derivatives have emerged. The careful choice of ligand and base proved to be decisive; the scheme shows one variation of one of the methods, which leads to amino esters. These results confirm, yet again, that the repertoire of palladium catalysis continues to expand at an astonishing pace.



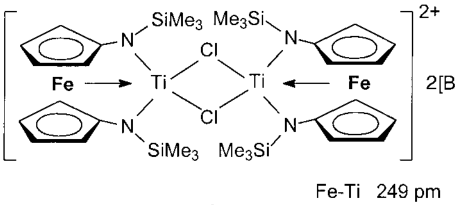
*Angew. Chem.* **2002**, *114*, 995–998

G. C. Lloyd-Jones* ........... 953–956

Palladium-Catalyzed $\alpha$-Arylation of Esters: Ideal New Methodology for Discovery Chemistry

**Keywords:** amino acids · arylation · esters · homogeneous catalysis · palladium · synthetic methods

**The search for catalysts** for olefin polymerization has brought complexes into the limelight that contain anionic 1,1′-ferrocenedi(amido) chelate ligands. The stabilization of cationic titanium centers by such a chelate ligand may lead to the formation of a dative Fe→Ti heterodimetallic bond, as in the cation of the salt **1**.



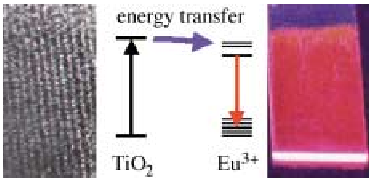
**1**

*Angew. Chem.* **2002**, *114*, 998–1000

M. Herberhold* .............. 956–958

1,1′-Ferrocenedi(amido) Chelate Ligands in Titanium and Zirconium Complexes

**Keywords:** amido ligands · chelates · ferrocenes · metal–metal interactions · sandwich complexes



**The well-ordered array of pores and walls** made up of nanocrystallites in a mesoporous titania thin film can be doped with high concentrations of Eu$^{3+}$ (up to 8 mol%) to create a bright red photoluminescent material (see picture). The photoluminescence arises from energy transfer through excitation of the titania nanocrystallites in their band gap to the crystal field states of the europium ions; photoluminescence concentration quenching is prevented because of the high surface area and nanocrystalline structure of the material.

*Angew. Chem.* **2002**, *114*, 1001 – 1004

K. L. Frindell, M. H. Bartl, A. Popitsch, G. D. Stucky* ................ 959 – 962

Sensitized Luminescence of Trivalent Europium by Three-Dimensionally Arranged Anatase Nanocrystals in Mesostructured Titania Thin Films

**Keywords:** europium · luminescence · mesoporous materials · nanocrystallites · titanium

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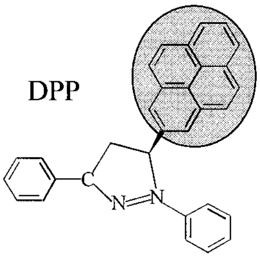

**Tunable, multiple emission** is exhibited by nanoparticles of 1,3-diphenyl-5-pyrenyl-2-pyrazoline (DPP; see picture), which ranges from near-UV to green. Tuning could be effected by alteration of either the excitation wavelength or the nanoparticle size. In contrast, DPP in dilute solution only showed the emission characteristics of the pyrene chromophore. In bulk crystals, only the emission characteristics of the pyrazoline chromophore were exhibited.

*Angew. Chem.* **2002**, *114*, 1004 – 1007

H. Fu, B. H. Loo, D. Xiao, R. Xie, X. Ji, J. Yao,* B. Zhang, L. Zhang ... 962 – 965

Multiple Emissions from 1,3-Diphenyl-5-pyrenyl-2-pyrazoline Nanoparticles: Evolution from Molecular to Nanoscale to Bulk Materials

**Keywords:** charge transfer · fluorescence · nanostructures · photochemistry

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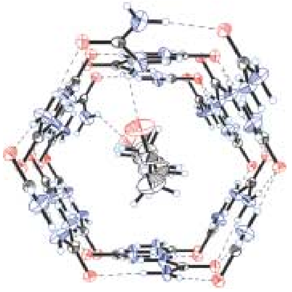
# VIPs

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

| | | |
|---|---|---|
| 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* | |
| Cyclo[8]pyrrole: A Simple-to-Make Expanded Porphyrin with No *meso* Bridges | D. Seidel, V. Lynch, J. L. Sessler* | |
| Cyclotetrasilenide Ion: A Reversible Redox System of Cyclotetrasilenyl Cation, Radical, and Anion | T. Matsuno, M. Ichinohe, A. Sekiguchi* | |

**Previously unrecognized chiral and rotational twinning** were revealed by optical microscopy, synchrotron white beam X-ray topography, and crystallography in the crystal structure of the inclusion compound of 2,12-tridecanedione/urea (see picture), which was otherwise intractable.



*Angew. Chem.* **2002**, *114*, 1007 – 1011

M. D. Hollingsworth,* M. E. Brown,
M. Dudley, H. Chung, M. L. Peterson,
A. C. Hillier . . . . . . . . . . . . . . . . . 965 – 969

Template Effects, Asymmetry, and Twinning in Helical Inclusion Compounds

**Keywords:** chirality • helical structures • inclusion compounds • polymorphism • X-ray diffraction

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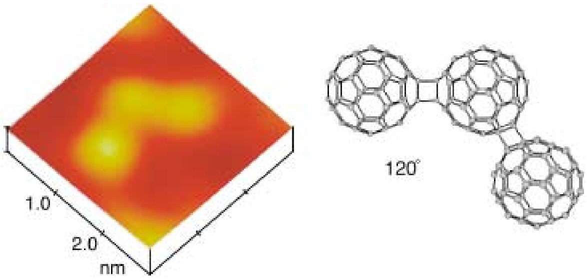
**Isomeric fullerene trimers** have been prepared by using a high speed vibration milling technique, and Langmuir films of the isomers observed on Au(111) surfaces by scanning tunneling microscopy (STM). Each isomer exhibited a different surface morphology. The observed distribution of isomers supports molecular orbital calculations of isomer stability. STM may be used to distinguish the individual isomers (see image), which is difficult to achieve by spectroscopy.



*Angew. Chem.* **2002**, *114*, 1011 – 1014

M. Kunitake,* S. Uemura, O. Ito,
K. Fujiwara, Y. Murata,
K. Komatsu* . . . . . . . . . . . . . . . . 969 – 972

Structural Analysis of $C_{60}$ Trimers by Direct Observation with Scanning Tunneling Microscopy

**Keywords:** fullerenes • nanotechnology • oligomers • scanning tunneling microscopy • solid-state reactions

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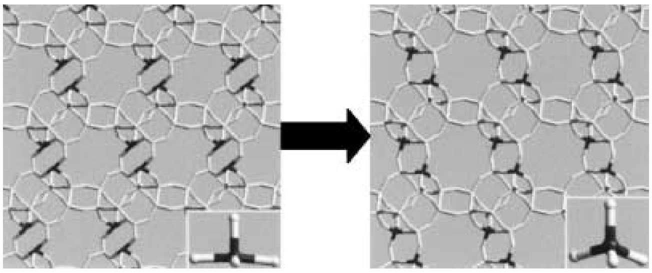
**Computer calcination**: The phase transformation of two as-synthesized fluorinated inorganic compounds into their related microporous structures upon calcination (see scheme) is predicted by using lattice energy minimizations, successfully capturing in one step dehydration, defluorination, and template elimination.



*Angew. Chem.* **2002**, *114*, 1014 – 1017

S. Girard, A. Tuel, C. Mellot-Draznieks,
G. Férey* . . . . . . . . . . . . . . . . . . . 972 – 975

Computational Prediction of the Phase Transformation of Two As-Synthesized Oxyfluorinated Compounds into the Zeotype CHA Forms

**Keywords:** aluminum • calcination • computer chemistry • microporous materials • zeolites

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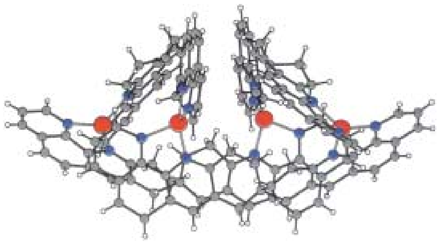
**Anthracene in a bucket**: Coordination-driven assembly of a ditopic ligand with copper salts leads to two stable tetranuclear complexes. The major complex, characterized by X-ray crystallography (see picture), displays a face-to-face arrangement of the phenanthroline subunits, and the inclusion of an anthracene molecule can be demonstrated by both proton NMR spectroscopy and cyclic voltammetry. The minor species has a plaited structure and does not exhibit significant interaction with the anthracene guest.



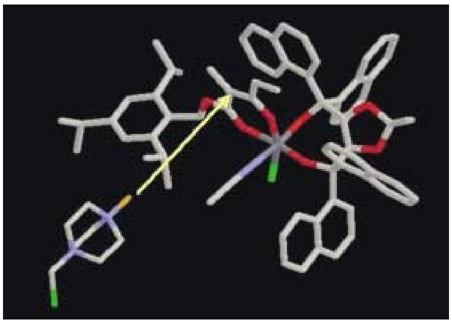
*Angew. Chem.* **2002**, *114*, 1017 – 1021

R. Ziessel,* L. Charbonnière, M. Cesario,
T. Prangé, H. Nierengarten . . . . 975 – 979

Assembly of a Face-to-Face Tetranuclear Copper(I) Complex as a Host for an Anthracene Guest

**Keywords:** copper • electrochemistry • host – guest systems • N ligands

**A parallel orientation** between the coordinated substrate enolate and a face-on naphthyl group of the TADDOL ligand (see picture; Ti dark gray, O red, Cl green, F orange, N violet) control the stereochemical outcome of the Ti-catalyzed asymmetric fluorination of 1,3-dicarbonyl compounds with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octanetriethylenediamine (F-TEDA; its approach is also shown the in picture). Density functional theory based quantum-mechanical molecular mechanical calculations also disclose the fluorine-transfer step as occurring by a single-electron transfer.



*Angew. Chem.* **2002**, *114*, 1021 – 1024

S. Piana, I. Devillers, A. Togni,*
U. Rothlisberger* ........... 979 – 982

The Mechanism of Catalytic Enantioselective Fluorination: Computational and Experimental Studies

**Keywords:** density functional calculations • electron transfer • fluorination • TADDOLs • titanium

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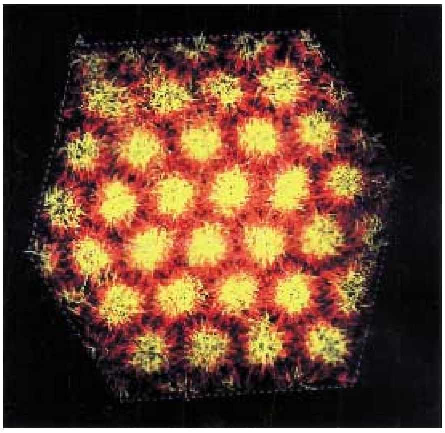
**Aggregation without aggravation**: A rapid and accurate estimation of the phase structure of amphiphilic molecules is made possible with a new computer simulation technique that excellently reproduces the aggregation behavior of such compounds. For dodecyldimethylamine oxide it is demonstrated how the micellar, hexagonal (see picture for isodensity profile), and lamella surfactant mesostructures can be calculated.



*Angew. Chem.* **2002**, *114*, 1025 – 1028

E. Ryjkina, H. Kuhn,* H. Rehage,
F. Müller, J. Peggau .......... 983 – 986

Molecular Dynamic Computer Simulations of Phase Behavior of Non-Ionic Surfactants

**Keywords:** amphiphiles • colloids • computer chemistry • micelles • molecular modeling

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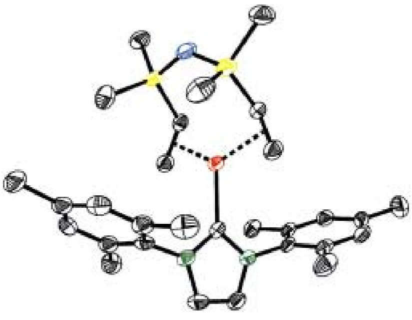
**Industrial reaction improved**: The first monocarbenepalladium(0) – olefin complex has been isolated and characterized (see structure; Pd orange, N green, S yellow, O blue). The complex exhibited unprecedented high catalyst productivity and selectivity for industrially important telomerization reactions (the dimerization of 1,3-dienes in the presence of a nucleophile, in this case an alcohol).



*Angew. Chem.* **2002**, *114*, 1028 – 1031

R. Jackstell, M. Gómez Andreu,
A. Frisch, K. Selvakumar, A. Zapf,
H. Klein, A. Spannenberg, D. Röttger,
O. Briel, R. Karch, M. Beller* 986 – 989

A Highly Efficient Catalyst for the Telomerization of 1,3-Dienes with Alcohols: First Synthesis of a Monocarbenepalladium(0) – Olefin Complex

**Keywords:** carbene ligands • homogeneous catalysis • palladium • telomerization

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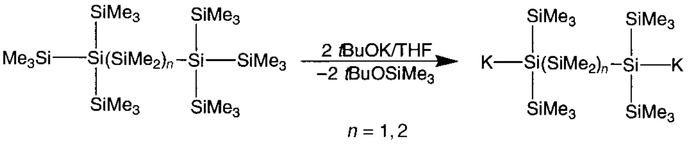
**Multiply metalated oligosilanes**: Treatment of bridged bis[tris(trimethylsilyl)silyl] compounds with two equivalents of potassium *tert*-butoxide leads to the formation of 1,3- and 1,4-dipotassium silanes [Eq. (1)]. Reaction of the latter with zirconocene dichloride and hafnocene dichloride, respectively, gives the corresponding metallacyclopentasilanes.



$$\mathrm{Me_3Si{-}\overset{SiMe_3}{\underset{SiMe_3}{Si}}(SiMe_2)_{\mathit{n}}{-}\overset{SiMe_3}{\underset{SiMe_3}{Si}}{-}SiMe_3 \xrightarrow[-2\,\mathit{t}BuOSiMe_3]{2\,\mathit{t}BuOK/THF} K{-}\overset{SiMe_3}{\underset{SiMe_3}{Si}}(SiMe_2)_{\mathit{n}}{-}\overset{SiMe_3}{\underset{SiMe_3}{Si}}{-}K} \qquad (1)$$

$n = 1, 2$

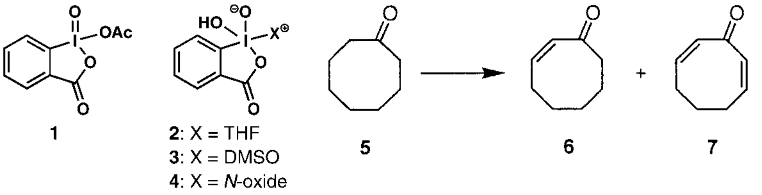
*Angew. Chem.* **2002**, *114*, 1031 – 1034

C. Kayser, G. Kickelbick,
C. Marschner* .............. 989 – 992

Simple Synthesis of Oligosilyl-$\alpha,\omega$-dipotassium Compounds

**Keywords:** dianions • silanes • Si ligands • silyl anions

**The reactivity profile of IBX** can be altered by complexation with various ligands (e.g. **1**–**4**). A new complex, IBX·MPO, is a remarkably effective oxidant and allows the room-temperature dehydrogenation of carbonyl compounds, for example, the formation of cyclooctenones **6** and **7** from cyclooctanone **5**. IBX = iodoxybenzoic acid; MPO = 4-methoxypyridine-*N*-oxide.



*Angew. Chem.* **2002**, *114*, 1035–1038

K. C. Nicolaou,* T. Montagnon,
P. S. Baran .................. 993–996

Modulation of the Reactivity Profile of IBX by Ligand Complexation: Ambient Temperature Dehydrogenation of Aldehydes and Ketones to $\alpha,\beta$-Unsaturated Carbonyl Compounds

**Keywords:** dehydrogenation · enones · hypervalent compounds · iodine · oxidation · synthetic methods

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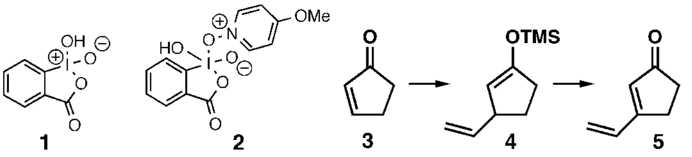
***α,β*-Unsaturated carbonyl compounds** can be prepared by the oxidation of trimethylsilyl enol ethers with IBX (**1**) or IBX·MPO (**2**). A diverse set of carbonyl compounds can be dehydrogenated with ease by using this method. Trimethylsilyl enol ethers such as **4**, which are formed in situ by the addition of an organometallic species to an enone, can be dehydrogenated with **1** or **2** to give a functionalized enone (e.g. **3**→**5**). IBX = iodoxybenzoic acid; MPO = 4-methoxypyridine-*N*-oxide.



*Angew. Chem.* **2002**, *114*, 1038–1042

K. C. Nicolaou,* D. L. F. Gray,
T. Montagnon, S. T. Harrison . 996–1000

Oxidation of Silyl Enol Ethers by Using IBX and IBX·*N*-Oxide Complexes: A Mild and Selective Reaction for the Synthesis of Enones

**Keywords:** dehydrogenation · enols · hypervalent compounds · iodine · oxidation · synthetic methods

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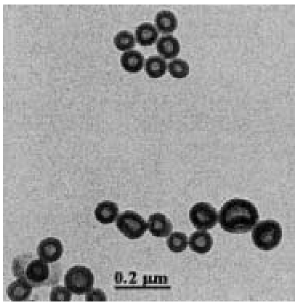
**By varying the hydrophilic block lengths** in polystyrene diblock copolymers containing both polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) and polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P(4-VP)), vesicles can be prepared (see transmission electron micrograph) in which the PAA and P(4-VP) chains can be preferentially segregated on the inside and outside of the vesicles.



*Angew. Chem.* **2002**, *114*, 1043–1046

L. Luo, A. Eisenberg* ...... 1001–1004

One-Step Preparation of Block Copolymer Vesicles with Preferentially Segregated Acidic and Basic Corona Chains

**Keywords:** block copolymers · colloids · curvature stabilization · electron microscopy · vesicles

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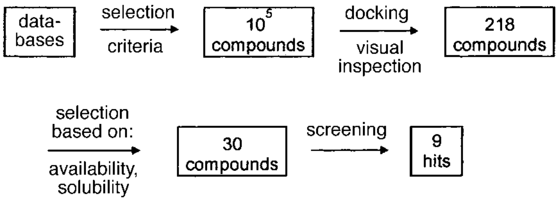
**Molecular docking** with a large number of guests, followed by experimental verification, was used to determine the selectivity of a synthetic host molecule and resulted in a hit rate of 30% (see schematic outline of procedure). The identification of ligands for a given receptor by means of screening may represent a paradigm shift in supramolecular host–guest chemistry.



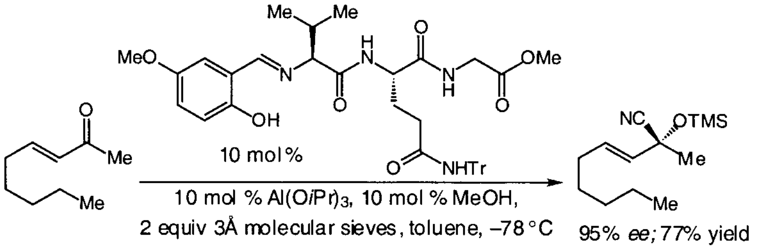
*Angew. Chem.* **2002**, *114*, 1046–1050

M. R. de Jong, R. M. A. Knegtel,
P. D. J. Grootenhuis, J. Huskens,*
D. N. Reinhoudt* ........... 1004–1008

A Method To Identify and Screen Libraries of Guests That Complex to a Synthetic Host

**Keywords:** computer chemistry · cyclodextrins · fluorescence spectroscopy · host–guest systems · screening

**Easily prepared peptide-based ligands** efficiently promote the Al-catalyzed enantioselective addition of trimethylsilyl cyanide (TMSCN) to aromatic, aliphatic, cyclic, and acyclic ketones (see scheme for an example). The chiral ligands can be readily recovered and reused without loss of activity or selectivity.



*Angew. Chem.* **2002**, *114*, 1051 – 1054

H. Deng, M. P. Isler, M. L. Snapper,*
A. H. Hoveyda* ........... 1009 – 1012

Aluminum-Catalyzed Asymmetric Addition of TMSCN to Aromatic and Aliphatic Ketones Promoted by an Easily Accessible and Recyclable Peptide Ligand

**Keywords:** addition · aluminum · asymmetric catalysis · asymmetric synthesis · cyanohydrins

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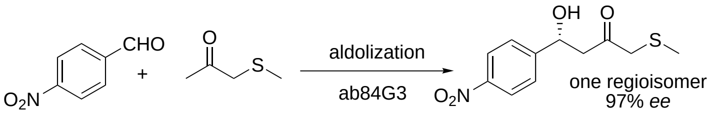
**Direct asymmetric aldol reactions at the less substituted carbon atom** of unmodified unsymmetrical ketones are achieved in the presence of the commercially available aldolase I antibody 84G3 [Eq. (1)]. All the reactions proceeded with enantiomeric excesses greater than 94%. Both enantiomers are accessible by using either an aldol or a retro-aldol reaction.



(1)

*Angew. Chem.* **2002**, *114*, 1054 – 1056

V. Maggiotti, M. Resmini,
V. Gouverneur* ........... 1012 – 1014

Unprecedented Regiocontrol Using An Aldolase I Antibody

**Keywords:** aldol reaction · asymmetric catalysis · catalytic antibodies · regioselectivity

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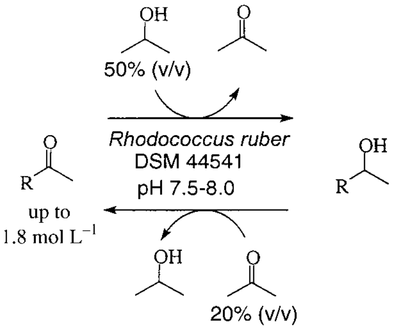
**Celling chemistry**: Ketones (secondary alcohols) can be biocatalytically reduced (oxidized) at a substrate concentration of up to 1.8 mol$L^{-1}$ in an asymmetric fashion by employing a novel secondary alcohol dehydrogenase from *Rhodococcus ruber* DSM 44541 (see scheme). Furthermore, the enzyme is exceptionally stable at high cosubstrate concentrations, that is, 2-propanol (50% v/v) for reduction and acetone (20% v/v) for oxidation, respectively.



*Angew. Chem.* **2002**, *114*, 1056 – 1059

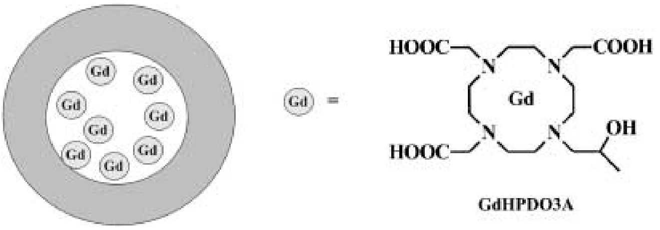
W. Stampfer, B. Kosjek, C. Moitzi,
W. Kroutil,* K. Faber ....... 1014 – 1017

Biocatalytic Asymmetric Hydrogen Transfer

**Keywords:** alcohols · biocatalysis · enzyme catalysis · hydrogen transfer · oxidoreductases

---

**A remarkably high relaxation enhancement** of water protons has been observed for solutions containing apoferritin loaded with GdHPDO3A (see schematic representation). The entrapment of the complex within apoferritin (internal diameter: 7.5 nm, external diameter: 12.5 nm) allows an increased number of dipolar interactions with water molecules and exchangeable protons in the protein cavity.



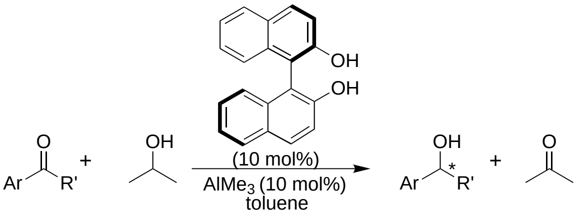
*Angew. Chem.* **2002**, *114*, 1059 – 1061

S. Aime,* L. Frullano,
S. Geninatti Crich .......... 1017 – 1019

Compartmentalization of a Gadolinium Complex in the Apoferritin Cavity: A Route To Obtain High Relaxivity Contrast Agents for Magnetic Resonance Imaging

**Keywords:** apoferritin · contrast agents · lanthanides · magnetic resonance imaging · relaxivity

**Efficient and practical**: An aluminum-based catalyst system for the asymmetric Meerwein–Schmidt–Ponndorf–Verley reduction of aromatic ketones is reported. By using *i*PrOH as the achiral hydride source and BINOL-type chiral ligands (see scheme), chiral secondary aromatic alcohols (up to 83 % *ee*) can be obtained in good yields.



*Angew. Chem.* **2002**, *114*, 1062–1064

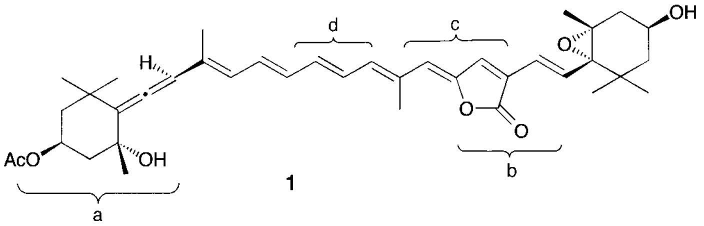
E. J. Campbell, H. Zhou,
S. T. Nguyen* ............. 1020–1022

The Asymmetric Meerwein–Schmidt–Ponndorf–Verley Reduction of Prochiral Ketones with *i*PrOH Catalyzed by Al Catalysts

**Keywords:** aluminum • asymmetric synthesis • homogeneous catalysis • ketones • reduction

---

**The convergent, highly stereoselective synthesis** of the nor carotenoid peridinin (**1**) is based on the following key steps: a) a Sharpless asymmetric epoxidation, b) reaction with a silylfuran-Wittig reagent and oxidation with $^1O_2$, c) a Pd-catalyzed three-step one-pot procedure for the formation of the ylidene butenolide segment), and d) a modified Julia olefination. This provides a new method for the synthesis of carotenoids.



**1**

*Angew. Chem.* **2002**, *114*, 1065–1068

N. Furuichi, H. Hara, T. Osaki, H. Mori,
S. Katsumura* ............ 1023–1026

Highly Efficient Stereocontrolled Total Synthesis of the Polyfunctional Carotenoid Peridinin

**Keywords:** asymmetric synthesis • carotenoids • diastereoselectivity • synthetic methods • total synthesis

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**A deep hole trap** is 7-deazaguanine (Z)—according to time-resolved transient absorption spectroscopy and kinetic modeling—for hole transport in DNA from a guanine (G) to a Z base across one or two intervening adenine–thymine base pairs. The Gibbs energy for hole transport from G to Z was determined to be −0.19 eV, much larger than values for GG or GGG sites. Thus Z effectively prevents charge migration in DNA.

*Angew. Chem.* **2002**, *114*, 1068–1070

F. D. Lewis,* J. Liu, X. Liu, X. Zuo,
R. T. Hayes,
M. R. Wasielewski* ........ 1026–1028

Dynamics and Energetics of Hole Trapping in DNA by 7-Deazaguanine

**Keywords:** DNA conjugates • electron transfer • photooxidation • picosecond spectroscopy

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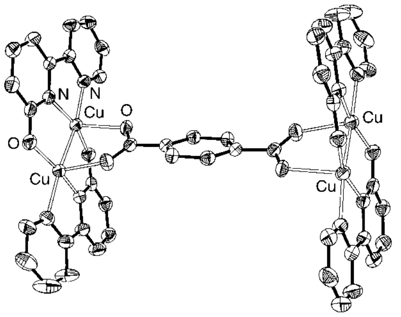
**Structural evidence for the Gillard mechanism** of covalent hydrates is provided by two mixed-valence $Cu^I$/$Cu^{II}$ complexes containing 2,2′-bipyridine (see picture) or 1,10-phenanthroline ligands, in which a hydroxy group is added to a carbon atom adjacent to a nitrogen atom. These complexes are synthesized by hydrothermal treatment of $Cu(NO_3)_2$, the respective N,N ligand, and terephthalic acid.



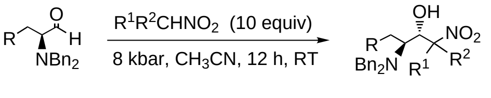
*Angew. Chem.* **2002**, *114*, 1071–1073

X.-M. Zhang, M.-L. Tong,
X.-M. Chen* .............. 1029–1031

Hydroxylation of N-Heterocycle Ligands Observed in Two Unusual Mixed-Valence $Cu^I$/$Cu^{II}$ Complexes

**Keywords:** copper • hydroxylation • mixed-valent compounds • N ligands • reaction mechanisms

**Under pressure**, the nitro-aldol reaction of (*S*)-*N*,*N*-dibenzylphenylalaninal and related compounds with nitroalkanes was highly stereoselective (see scheme; $R^1$, $R^2$ = Me, H; R = Ph, Me, *i*Pr, *i*Bu). This reaction is very convenient, as it only requires high pressure and no catalyst.



*Angew. Chem.* **2002**, *114*, 1073 – 1075

Y. Misumi, K. Matsumoto* . 1031 – 1033

### Diastereoselective Asymmetric Nitro-Aldol Reaction of $\alpha$-Amino Aldehydes under High Pressure without Catalyst

**Keywords:** addition • amino alcohols • asymmetric synthesis • diastereoselectivity • high-pressure chemistry • synthetic methods

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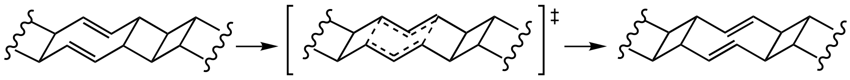
**A new (and so far hypothetical) class of molecules** is described—the "sigmatropic shiftamers." These are polymers that contain local "defects"—single or double bonds—which propagate by sigmatropic rearrangements (see scheme).



*Angew. Chem.* **2002**, *114*, 1075 – 1078

D. J. Tantillo, R. Hoffmann* 1033 – 1036

### Sigmatropic Shiftamers: Fluxionality in Broken Ladderane Polymers

**Keywords:** Cope rearrangement • ladderanes • polymers • rearrangement • transition states

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**A uniform pore size with a highly ordered structure** is still observed for zeolite (ZSM-5)-coated mesoporous aluminosilicates (ZCMesoAS) even after the coating procedure (see transmission electron micrograph). These ZCMesoAS, which are hydrothermally ultrastable and highly acidic owing to the nanocrystalline zeolitic nature of their pore wall surface, are produced from diluted clear solutions containing primary zeolite units. The novel features of ZCMesoAS open new possibilities for their use as acid catalysts.

*Angew. Chem.* **2002**, *114*, 1078 – 1082

D. Trong On, S. Kaliaguine* 1036 – 1040

### Ultrastable and Highly Acidic, Zeolite-Coated Mesoporous Aluminosilicates

**Keywords:** mesoporous materials • nanostructures • solid-state reactions • zeolites

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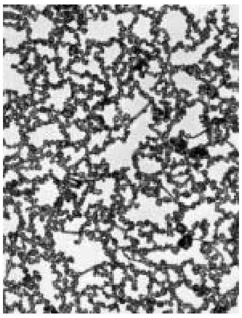
**The concentration of the plating solution** enables control over the fine-tuning of fractal patterns and also drastically affects the crystal growth of Ag/Au core – shell roughened nanoparticles through diffusion-limited aggregation. At low concentrations there are more open spaces in the well-ramified fractal pattern than at higher concentrations, and the whisker-linked nanoparticles align almost one-by-one (see transmission electron micrograph).



*Angew. Chem.* **2002**, *114*, 1082 – 1086

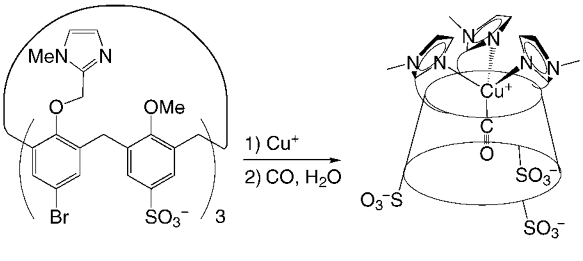
Y. Jin, S. Dong* ............ 1040 – 1044

### Diffusion-Limited, Aggregation-Based, Mesoscopic Assembly of Roughened Core-Shell Bimetallic Nanoparticles into Fractal Networks at the Air-Water Interface

**Keywords:** aggregation • electron microscopy • fractals • nanoparticles

---

**Remarkable stabilization** of a copper(I) center is evident in the tris(sulfonated) calixarene-based complex shown. This complex is truly biomimetic as it is soluble in water and also has a free valence where CO can bind. Thus it imitates the first coordination sphere encountered in copper enzymes and the hydrophobic microenvironment of the active site.



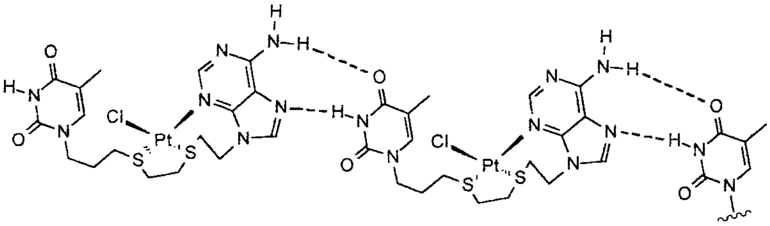
*Angew. Chem.* **2002**, *114*, 1086 – 1088

Y. Rondelez, G. Bertho,
O. Reinaud* .............. 1044 – 1046

### The First Water-Soluble Copper(I) Calix[6]arene Complex Presenting a Hydrophobic Ligand Binding Pocket: A Remarkable Model for Active Sites in Metalloenzymes

**Keywords:** calixarenes • copper • enzyme models • host – guest systems • solvent effects

**Hoogsteen base pairing** between coordinated adenine (A) and pendant thymine (T) residues of the Pt complex of a dithioether ligand bearing A and T groups results in the formation of infinite chains in the solid state (see picture). The chains are further involved in π–π stacking interactions.



Angew. Chem. **2002**, *114*, 1089–1091

C. Price, B. R. Horrocks, A. Mayeux,
M. R. J. Elsegood, W. Clegg,
A. Houlton* .............. 1047–1049

Self-Complementary Metal Complexes Containing a DNA Base Pair

**Keywords:** chain structures · hydrogen bonds · nucleobases · self-assembly · S ligands

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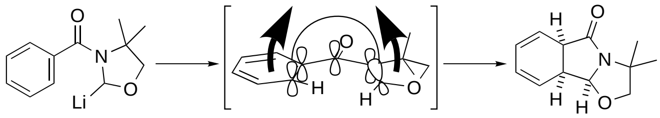
**Loss of aromaticity** ensues when *N*-benzoyl oxazolidines are lithiated and undergo a 6π disrotatory electrocyclization (see scheme). The stereochemistry of the cyclization shows it to be a new example of an electrocyclic ring closure. The *cis*-tricyclic products epimerize to their more stable *trans* diastereoisomers in aqueous acid.



Angew. Chem. **2002**, *114*, 1091–1093

J. Clayden,* S. Purewal, M. Helliwell,
S. J. Mantell ................ 1049–1051

Dearomatizing Disrotatory Electrocyclic Ring Closure of Lithiated *N*-Benzoyloxazolidines

**Keywords:** amides · cyclization · lithiation · pericyclic reaction · stereoselectivity

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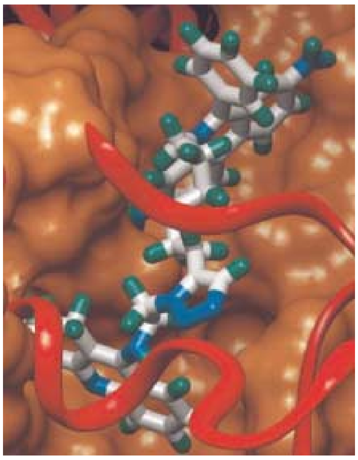
**Form-fitting chemistry in a protein mold** is enabled by the use of the 1,3-dipolar cycloaddition of azides and alkynes. The enzyme acetylcholinesterase preferentially assembles one pair of these reactants, each of which bears a group that binds to adjacent positions on the protein structure (see picture), into a 1,2,3-triazole adduct that is the most potent noncovalent inhibitor of the enzyme yet developed.



Angew. Chem. **2002**, *114*, 1095–1098

W. G. Lewis, L. G. Green, F. Grynszpan,
Z. Radić, P. R. Carlier,
P. Taylor, M. G. Finn,*
K. B. Sharpless* ........... 1053–1057

Click Chemistry In Situ: Acetylcholinesterase as a Reaction Vessel for the Selective Assembly of a Femtomolar Inhibitor from an Array of Building Blocks

**Keywords:** combinatorial chemistry · cycloaddition · heterocycles · hydrolases · inhibitors

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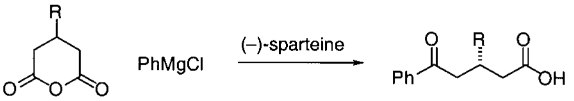
**Where other common chiral ligands failed**, (−)-sparteine can be employed to form complexes with Grignard reagents. These chirally modified reagents desymmetrize a range of anhydrides with good enantioselectivity (up to 92% *ee*; see scheme). Whereas (−)-sparteine is well known to form complexes with organolithium reagents and to induce excellent enantioselection in their reactions with electrophiles, (−)-sparteine-controlled asymmetric processes that involve Grignard reagents are rare.



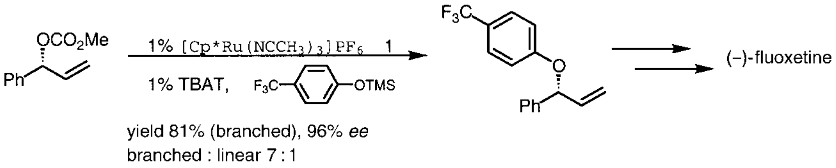
Angew. Chem. **2002**, *114*, 1099–1101

R. Shintani, G. C. Fu* ...... 1057–1059

Highly Enantioselective Desymmetrization of Anhydrides by Carbon Nucleophiles: Reactions of Grignard Reagents in the Presence of (−)-Sparteine

**Keywords:** anhydrides · asymmetric synthesis · desymmetrization · Grignard reaction

**Good regioselectivity and chirality transfer** for aryl-substituted allyl units is achieved in allylic alkylations with a wide range of nucleophiles by using the highly active ruthenium catalyst **1**. This method provides a route to antidepressants such as (−)-fluoxetine from (*S*)-ephedrine (see scheme; $Cp^* = \eta^5\text{-}C_5Me_5$, TBAT = tetrabutylammonium triphenyldifluorosilicate).



yield 81% (branched), 96% *ee*
branched : linear 7 : 1

*Angew. Chem.* **2002**, *114*, 1101–1103

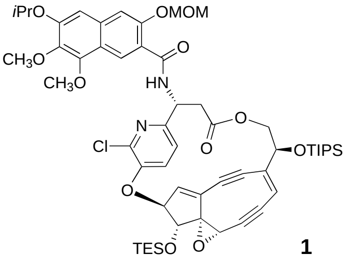
B. M. Trost,* P. L. Fraisse, Z. T. Ball .................. 1059–1061

A Stereospecific Ruthenium-Catalyzed Allylic Alkylation

**Keywords:** alkylation · allylic compounds · chirality transfer · homogeneous catalysis · regioselectivity · ruthenium

---

**Four components, each prepared in multigram amounts**, have been assembled in the convergent (25 steps in the longest linear sequence), enantioselective synthesis of the differentially protected kedarcidin chromophore aglycon (**1**). In addition to the enantioselective synthesis of each of the four components, the route features a transannular anionic cyclization to form the bicyclo[7.3.0]dodecadienediyne core in the presence of an ansa-bridged macrolactone. MOM = methoxymethyl, TIPS = triisopropylsilyl, TES = triethylsilyl.



**1**

*Angew. Chem.* **2002**, *114*, 1104–1109

A. G. Myers,* P. C. Hogan, A. R. Hurd, S. D. Goldberg ............ 1062–1067

Enantioselective Synthesis of Kedarcidin Chromophore Aglycon in Differentially Protected Form

**Keywords:** aglycons · antibiotics · asymmetric synthesis · cyclization · enediynes

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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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