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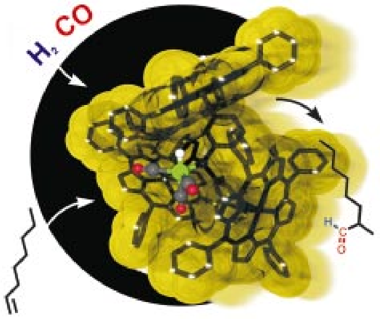
# COVER PICTURE

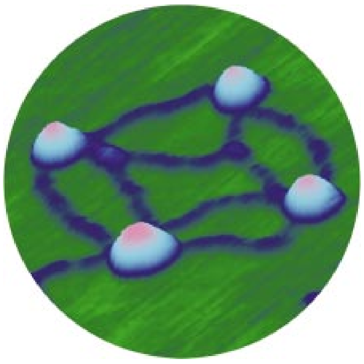
**The cover picture shows** a rhodium catalyst (green) that is encapsulated by three porphyrin molecules (black; the van der Waals radii are shown in yellow). The hemispherical assembly is obtained by a self-assembly process using readily available pyridylphosphane and zinc-porphyrin building blocks. Its exclusive formation is based on selective coordination of the nitrogen atom to the zinc atom and the phosphane group to the rhodium center. The catalyst assemblies show a higher activity than the free rhodium catalyst in the rhodium-catalyzed hydroformylation of 1-octene, and the branched product is now the main product. In a similar way, the assembly of porphyrin building blocks to pyridylphosphane can regulate the performance of palladium catalysts in the Heck reaction. Further details about these catalyst assemblies can be found in the article by Reek et al. on p. 4271 ff.



# REVIEW

Contents

**At the crossroads** of biotechnology, nanoscience, and materials research lies a new interdisciplinary research area, in which the use of evolutionary optimized biomolecules for the development of advanced materials and analytical procedures is investigated. As an example, nanoparticles can be interconnected with DNA to generate nanostructured hybrid materials (see scanning force microscopy image).



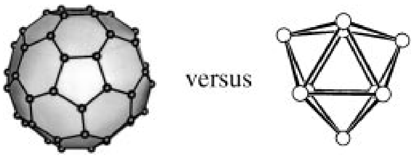
*Angew. Chem.* **2001**, *113*, 4254–4287

C. M. Niemeyer* ........... 4128–4158

Nanoparticles, Proteins, and Nucleic Acids: Biotechnology Meets Materials Science

**Keywords:** analytical methods · biotechnology · materials science · nanostructures · supramolecular chemistry

## MINIREVIEW



**There is a common feature** between the two recently synthesized polymers $^1_\infty\{C_{70}^{2-}\}$ and $^1_\infty\{[Ge_9]^{2-}\}$: The successful linking of homoatomic anions into one-dimensional polymers opens up fantastic opportunities for the design and construction of nanostructures. A comparison between these structural modules (see schematic representation) shows that Zintl ions, which have been known for more than a hundred years, are in no way inferior to the fullerenes.

*Angew. Chem.* **2001**, *113*, 4289 – 4293

T. F. Fässler* .............. 4161 – 4165

Homoatomic Polyhedra as Structural Modules in Chemistry: What Binds Fullerenes and Homonuclear Zintl Ions?

**Keywords:** cage compounds · fullerenes · polymers · Zintl ions

## ESSAY

**Reality, or through the looking-glass?** In 1951 two important advances in structural chemistry were made: Pauling formulated the α-helix as an important structural element in proteins, and Bijvoet solved the problem of determining absolute configuration. This essay covers events binding these two discoveries.

*Angew. Chem.* **2001**, *113*, 4295 – 4301

J. D. Dunitz* ............. 4167 – 4173

Pauling's Left-Handed α-Helix

**Keywords:** biographies · history of science · stereochemistry · structure elucidation

## 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

| | | |
|---|---|---|
| Origin of Ferromagnetism in Cyano-Bridged Compounds Containing $d^1$ Octacyanometallates | L. F. Chibotaru,* V. S. Mironov, A. Ceulemans | ◆ |
| Lewis Acid/Base Stabilized Phosphanylalane and -gallane | U. Vogel, A. Y. Timoshkin, M. Scheer* | ◆ |
| Towards the Understanding of Solid-State Structures: From Cubic to Chain-like Arrangements in Group 11 Halides | T. Söhnel, H. Hermann, P. Schwerdtfeger* | ◆ |
| Homogeneous Reactions in Supercritical Carbon Dioxide by Using a Catalyst Immobilized in a Microporous Silica Membrane | L. J. P. van den Broeke,* E. L. V. Goetheer, A. W. Verkerk, E. de Wolf, B.-J. Deelman, G. van Koten, J. T. F. Keurentjes | ◆ |
| Design and Synthesis of a Peptide that Binds Specific DNA Sequences through Simultaneous Interaction in the Major and in the Minor Groove | M. E. Vázquez, A. M. Caamaño, J. Martínez-Costas, L. Castedo, J. L. Mascareñas* | |
| Cesiumauride Ammonia (1/1: $CsAu \cdot NH_3$)—A Crystalline Analogue of Alkali Metals Dissolved in Ammonia? | A.-V. Mudring, M. Jansen,* J. Daniels, S. Krämer, M. Mehring, J. P. Ramalho, A. H. Romero, M. Parrinello | |
| Enantiopure Double-Helical Acetylenic Cyclophanes | D.-L. An, T. Nakano, A. Orita, J. Otera* | |
| Supramolecular Cluster Catalysis: A Case Study of Benzene Hydrogenation Catalyzed by a Cationic Triruthenium Cluster under Biphasic Conditions | G. Süss-Fink,* M. Faure, T. R. Ward | |

1433-7851/01/4022-4112 $ 17.50+.50/0

# HIGHLIGHT

**From genome data to a successful drug**: Many companies are eager to make this journey in the future, though roadmaps are still scarce. We comment on a novel method that promises to make the trip from gene to drug (see schematic representation) shorter and more effective by predicting protein functions from their three-dimensional structure.

*Angew. Chem.* **2001**, *113*, 4303–4305

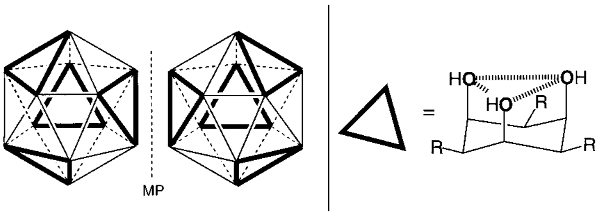
G. Folkers,* C. D. P. Klein ... 4175–4177

Computational Methods Facilitate the Assignment of Protein Functions

**Keywords:** bioinformatics · drug research · functional genomics · molecular modeling · proteome analysis

# COMMUNICATIONS

**A homoleptic metal complex** with four tripodal tridentate ligands can have chiral tetrahedral *T* symmetry. An example of such a complex has been prepared, and the proposed highly symmetric, but chiral structure (see schematic representation, MP = mirror plane, R = $NHCH_2PH$) has been confirmed.



*Angew. Chem.* **2001**, *113*, 4307–4310

J. Sander, K. Hegetschweiler,* B. Morgenstern, A. Keller, W. Amrein, T. Weyhermüller, I. Müller 4179–4182

*T*-Symmetrical Icosahedra: A New Type of Chirality in Metal Complexes

**Keywords:** chelates · chirality · group theory · structure elucidation · tripodal ligands

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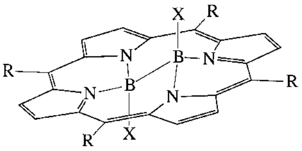
**Fitting $B_2$ bridges in porphyrins** (see picture) can be achieved by reaction of dilithiated porphyrins with $B_2Cl_4$ as well as by reductive elimination from diborylporphyrins. Coordination takes place under rectangular distortion of the porphyrin framework.



*Angew. Chem.* **2001**, *113*, 4311–4313

A. Weiss, H. Pritzkow, P. J. Brothers,* W. Siebert* ................ 4182–4184

Coordinated $B_2$ Bridges in Porphyrins—Unexpected Formation of a Diborane(4)- from a Diborylporphyrin

**Keywords:** boron · diboranes · N ligands · porphyrinoids

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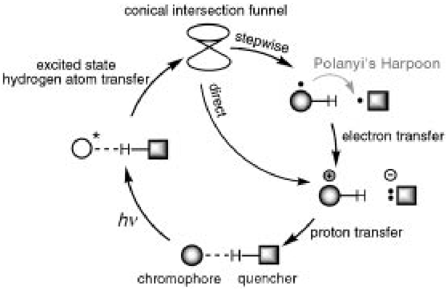
**Radical-pair disproportionation** through sequential electron–proton transfer (Polanyi's harpoon) is one efficient mechanism leading to quenching fluorescence of n,π*-excited states by hydrogen donors. This mechanism is demonstrated by ab initio MS-CASPT2 calculations and experimental investigations (photoproduct studies and EPR spin-trapping experiments) on the quenching of singlet-excited azoalkanes by chlorinated hydrocarbons.



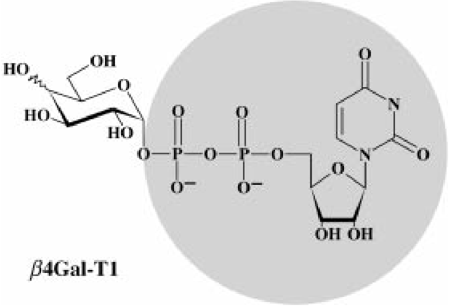
*Angew. Chem.* **2001**, *113*, 4313–4318

A. Sinicropi, R. Pogni,* R. Basosi, M. A. Robb, G. Gramlich, W. M. Nau,* M. Olivucci* ............... 4185–4189

Fluorescence Quenching by Sequential Hydrogen, Electron, and Proton Transfer in the Proximity of a Conical Intersection

**Keywords:** ab initio calculations · conical intersections · electron transfer · fluorescence quenching · proton transfer

**Saturation transfer difference (STD) NMR experiments** reveal the binding epitopes of UDP-Gal and UDP-Glc bound to the glycosyltransferase β4Gal-T1 (see picture). Whereas the enzyme recognizes the galactose residue in UDP-Gal, it does not make any close contacts with the glucose residue in UDP-Glc. This observation explains why β4Gal-T1 binds to UDP-Glc but is unable to transfer glucose to an acceptor substrate.



*Angew. Chem.* **2001**, *113*, 4320–4323

T. Biet, T. Peters* .......... 4189–4192

Molecular Recognition of UDP-Gal by β-1,4-Galactosyltransferase T1

**Keywords:** carbohydrates · glycoproteins · molecular recognition · NMR spectroscopy · transferases

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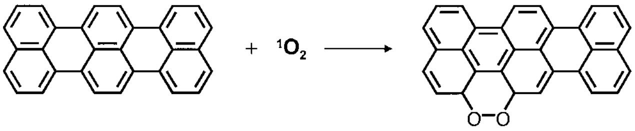
**The photooxidation of single dye molecules** (see scheme) can be followed by confocal fluorescence microscopy. The self-sensitized reaction with singlet oxygen leads to a suite of products, which may be differentiated spectrally. Tentative structures for certain photoproducts have been obtained from quantum-chemical calculations.



*Angew. Chem.* **2001**, *113*, 4323–4326

T. Christ, F. Kulzer, P. Bordat,
T. Basché* ................ 4192–4195

Watching the Photo-Oxidation of a Single Aromatic Hydrocarbon Molecule

**Keywords:** fluorescence spectroscopy · photochemistry · single-molecule spectroscopy

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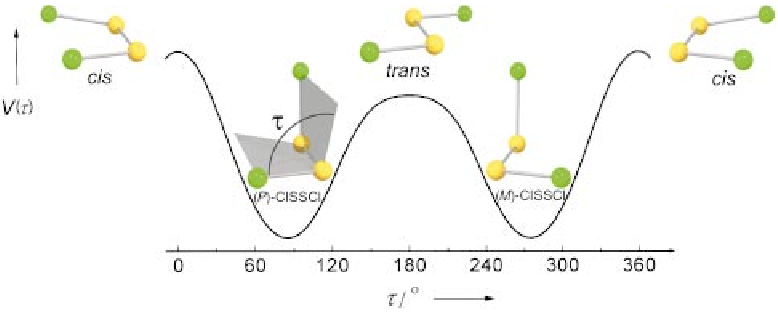
**Meaninglessly small** would be the effects from parity violation according to the traditional point of view on the structure and dynamics of chiral molecules; enantiomers would thus exist as symmetry-related structures, which are de facto stable because of very long tunneling times. With ClSSCl as the first example, electroweak and tunneling dynamics calculations demonstrate that the de lege asymmetry arising from the parity-violating energy difference $\Delta E_{pv}$ between the two enantiomers ((*P*)- and (*M*)-ClSSCl, the figure shows the torsional potentials) dominates by far over the tunneling splitting in the symmetrical case. These results are of fundamental interest for our concept of molecular chirality.



*Angew. Chem.* **2001**, *113*, 4342–4345

R. Berger, M. Gottselig, M. Quack,*
M. Willeke ................ 4195–4198

Parity Violation Dominates the Dynamics of Chirality in Dichlorodisulfane

**Keywords:** ab initio calculations · chirality · electroweak interactions · parity violation · torsional tunneling splitting

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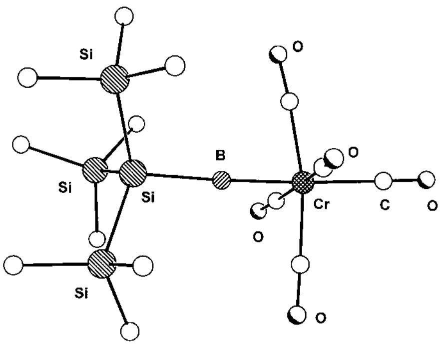
**An extremely low-field shifted $^{11}$B NMR signal** at $\delta = 204.3$ and a very short Cr–B distance of 187.8 pm characterize the title compound $[(OC)_5Cr{=}B{-}Si(SiMe_3)_3]$ (see structure), which is the first borylene complex in which the boron atom is both coordinatively and electronically unsaturated.



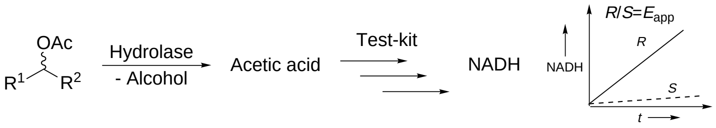
*Angew. Chem.* **2001**, *113*, 4327–4329

H. Braunschweig,* M. Colling,
C. Kollann, K. Merz,
K. Radacki ................ 4198–4200

$[(OC)_5Cr{=}BSi(SiMe_3)_3]$: A Terminal Borylene Complex with an Electronically Unsaturated Boron Atom

**Keywords:** B ligands · boron · borylene complexes · chromium

**A rapid and reliable test** for the determination of hydrolase activity and enantioselectivity comprises the conversion of acetic acid released from acetates to NADH by using a commercially available enzymatic test-kit (see scheme). The NADH is spectrophotometrically quantified in a microtiter plate format.



*Angew. Chem.* **2001**, *113*, 4329–4333

M. Baumann, R. Stürmer,
U. T. Bornscheuer* ........ 4201–4204

A High-Throughput-Screening Method for the Identification of Active and Enantioselective Hydrolases

**Keywords:** biotransformations · enantioselectivity · enzyme catalysis · high-throughput screening · molecular evolution

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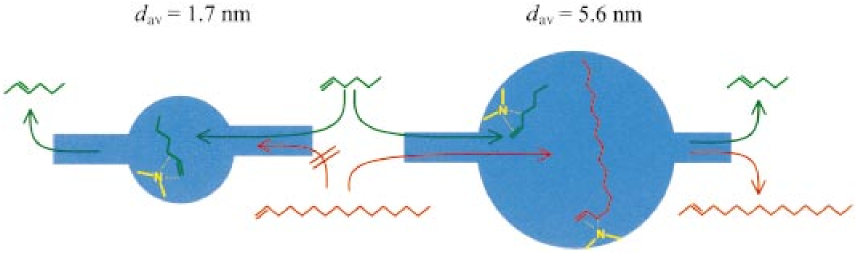
**High specific surface areas** and adjustable pore sizes are outstanding characteristics of nanoporous silicon nitride based materials prepared by using oxygen-free molecular precursors in a novel template-assisted sol–gel approach. The nitrides represent a new class of shape-selective superbase catalysts (see, for example, the schematic representation of alkene isomerization).



*Angew. Chem.* **2001**, *113*, 4336–4339

D. Farrusseng, K. Schlichte, B. Spliethoff,
A. Wingen, S. Kaskel,* J. S. Bradley,
F. Schüth .................. 4204–4207

Pore-Size Engineering of Silicon Imido Nitride for Catalytic Applications

**Keywords:** heterogeneous catalysis · microporous materials · nitrides · silicon · solid-state reactions · superbases

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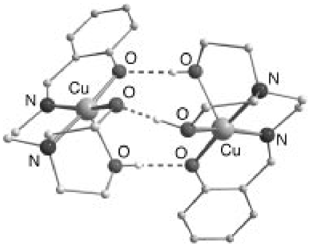
**The self-complementary coordination unit** $[Cu(H_2sabhea)]^+$ with a pentadentate amino alcohol as ligand enables the synthesis of the first triply hydrogen-bridged dinuclear copper(II) complex (see picture). Proton transfer allows the reversible transformation between this triply and the corresponding doubly hydrogen-bridged form. Despite the very short hydrogen bond found for the triply bridged complex, its exchange coupling constant is much smaller than that for the doubly bridged complex. $H_3sabhea$ = *N*-salicylidene-2-(bis(2-hydroxyethyl)amino)ethyl amine.



*Angew. Chem.* **2001**, *113*, 4333–4336

W. Plass,* A. Pohlmann,
J. Rautengarten ............. 4207–4210

Magnetic Interactions as Supramolecular Function: Structure and Magnetic Properties of Hydrogen-Bridged Dinuclear Copper(II) Complexes

**Keywords:** copper · density functional calculations · hydrogen bonds · magnetic properties · supramolecular chemistry

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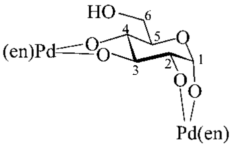
**The most important monosaccharide**—and not a single structurally characterized transition metal complex. That is the actual situation regarding basis data for understanding or designing metal-catalyzed reactions of D-glucose. This oversight is remedied with a palladium(II) complex and a structural analysis (see picture, en = ethylenediamine).



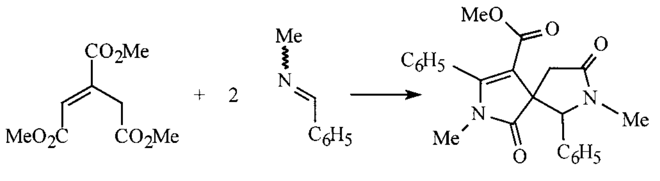
*Angew. Chem.* **2001**, *113*, 4356–4358

P. Klüfers,* T. Kunte ........ 4210–4212

A Transition Metal Complex of D-Glucose

**Keywords:** carbohydrates · glucose · palladium · structure elucidation

**The multitalented synthetic reagent** trimethyl aconitate (**1**) is a renewable raw material with a high density of functional groups that up to now has only been scarcely used as a $C_6$ building block. Domino reactions with **1** consisting of imine additions and intramolecular acylations provide simple access to heteropolycycles in one-pot reactions. For example, **1** reacts with *N*-methylbenzylidenamine (**2**) to give the spiro[pyrrolidinone-3,3′-dihydropyrrolinone] **3** in 40% yield (see scheme).



**1** **2** **3**

*Angew. Chem.* **2001**, *113*, 4354–4356

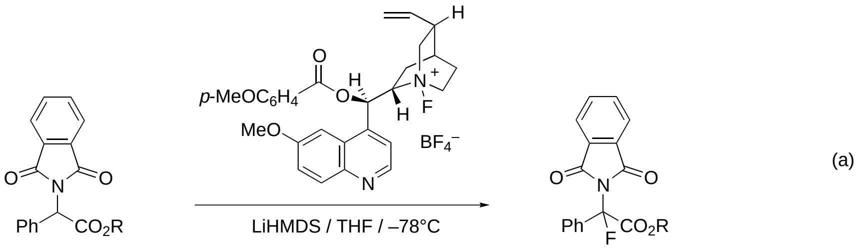
D. Witthaut, R. Fröhlich,
H. J. Schäfer* ............ 4212–4214

Heterocycles through Domino Reactions with Trimethyl Aconitate, a Versatile Synthetic Building Block

**Keywords:** acylation · domino reactions · imines · nitrogen heterocycles · spiro compounds

---

**A decisive step forward**: A one-step fluorination on modified cinchona alkaloids produced a new range of enantiopure fluorinating agents that display high enantioselectivities in electrophilic fluorination. The first enantioselective synthesis of *N*-protected $\alpha$-fluorophenylglycine derivatives was achieved with an enantiomeric excess up to 94% [Eq. (a); R = Et, CN; HMDS = hexamethyldisilazanide].



*Angew. Chem.* **2001**, *113*, 4339–4341

B. Mohar, J. Baudoux, J.-C. Plaquevent,
D. Cahard* ............... 4214–4216

Electrophilic Fluorination Mediated by Cinchona Alkaloids: Highly Enantioselective Synthesis of $\alpha$-Fluoro-$\alpha$-phenylglycine Derivatives

**Keywords:** alkaloids · amino acids · asymmetric synthesis · fluorination · fluorine

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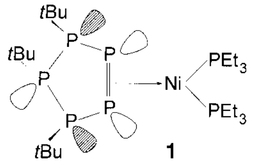
**Forming a phosphorus envelope**: The first structurally characterized cyclooligophosphanide ion [*cyclo*-($P_5t$$Bu_4$)]$^-$ to be obtained by a targeted synthesis reacts with [$NiCl_2(PEt_3)_2$] by loss of a *t*Bu group to give ($\eta^2$-3,4,5-tri-*tert*-butylcyclopentaphosphene)bis(triethylphosphane)nickel(0) (**1**). The previously unknown cyclopentaphosphene ring in **1** has an envelope conformation in solution and in the solid state, and the *t*Bu groups adopt an *all-trans* configuration.



*Angew. Chem.* **2001**, *113*, 4345–4348

A. Schisler, P. Lönnecke,
U. Huniar, R. Ahlrichs,
E. Hey-Hawkins* .......... 4217–4219

Sodium Tetra-*tert*-butylcyclopentaphosphanide: Synthesis, Structure, and Unexpected Formation of a Nickel(0) Tri-*tert*-butylcyclopentaphosphene Complex

**Keywords:** nickel · phosphorus heterocycles · P ligands

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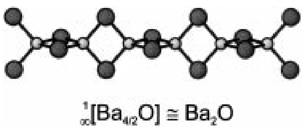
**Linear $^1_\infty$[Ba$_{4/2}$O] chains** (see picture) of edge-sharing $Ba_4O$ tetrahedra are separated by sodium atoms in the crystal structure of the new sodium barium suboxide $NaBa_2O$. The metal-rich compound is held together by a combination of ionic and metallic bonding according to the formulation $Na^+(Ba^{2+})_2O^{2-} \cdot 3e^-$.



*Angew. Chem.* **2001**, *113*, 4348–4351

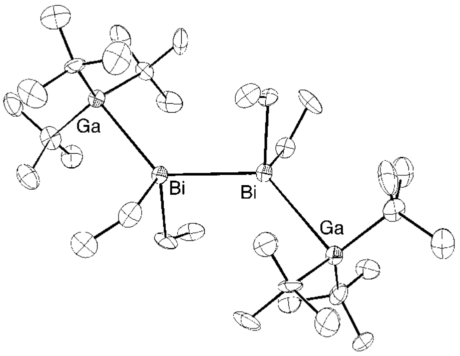
G. V. Vajenine, A. Simon* .. 4220–4222

$NaBa_2O$: A Fresh Perspective in Suboxide Chemistry

**Keywords:** barium · sodium · suboxides · subvalent compounds

1433-7851/01/4022-4116 $ 17.50+.50/0

**Functioning as a bidentate ligand** toward Lewis acids, dibismuthane forms bisadducts of the type $[R_3M]_2[Bi_2R'_4]$ with $R_3M = t\mathrm{Bu}_3\mathrm{Al}$ (**1**) and $t\mathrm{Bu}_3\mathrm{Ga}$ (**2;** structure depicted; $R' = \mathrm{Et}$), which were characterized by single-crystal X-ray diffraction.



*Angew. Chem.* **2001**, *113*, 4351–4353

A. Kuczkowski, S. Schulz,*
M. Nieger .................. 4222–4225

Reactions of $\mathrm{Et_4Bi_2}$ with $t\mathrm{Bu_3M}$ (M = Al, Ga)—Synthesis of Complexes with a Bidentate Dibismuthane Ligand

**Keywords:** adducts • aluminum • bismuth • gallium

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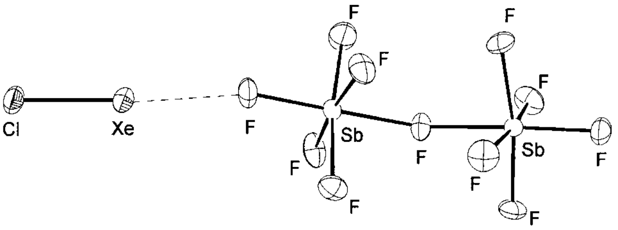
**Chlorine–fluorine exchange in $\mathrm{XeF^+}$** leads to the orange crystalline salt $\mathrm{[XeCl]^+[Sb_2F_{11}]^-}$ (see structure), which is stable below −10°C. Thus, the number of known noble gas monohalogen cations is now three and, as calculations show, is approaching the theoretically possible limit. The synthesis of other such compounds—with the exception of $\mathrm{ArF^+}$, which remains a formidable task—seems unlikely.



*Angew. Chem.* **2001**, *113*, 4318–4320

S. Seidel, K. Seppelt* ...... 4225–4227

The $\mathrm{XeCl^+}$ Ion: $\mathrm{[XeCl]^+[Sb_2F_{11}]^-}$

**Keywords:** ab initio calculations • chlorine • noble gas compounds • structure elucidation • xenon

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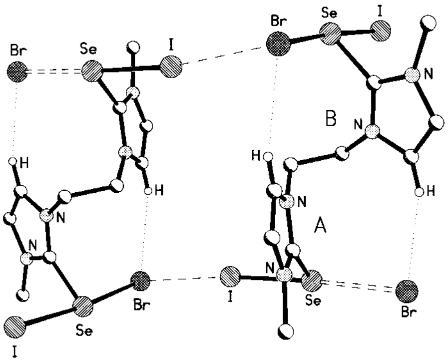
**Almost linear I-Se-Br groups** with $d(\mathrm{Se{-}Br}) > d(\mathrm{Se{-}I})$ occur in $\mathbf{1}\cdot 2\,\mathrm{IBr}$ (see structure), the first "T-shaped" Se adduct with IBr, which was synthesized by the oxidative addition of IBr to 1,2-bis(3-methylimidazoline-2-selonyl)ethane (**1**) in MeCN. Density functional theory calculations indicate the intramolecular Br···H interactions as being responsible for the peculiar structural features of the I-Se-Br groups.



*Angew. Chem.* **2001**, *113*, 4359–4362

M. C. Aragoni, M. Arca, A. J. Blake,
F. A. Devillanova,* W.-W. du Mont,
A. Garau, F. Isaia, V. Lippolis,* G. Verani,
C. Wilson .................. 4229–4232

1,2-Bis(3-methyl-imidazolin-2-ylium iodobromoselenanide)ethane: Oxidative Addition of IBr at the Se Atom of a >C=Se Group

**Keywords:** density functional calculations • donor–acceptor systems • halogens • hypervalent compounds • Se ligands

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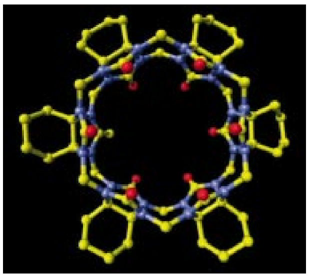
**Reminiscent of the ringed planet Saturn**, new cucurbit[*n*]uril (CB[*n*]) derivatives CB*[5] and CB*[6] have rings decorating the "equator". The rings in this case are five- and six-fused cyclohexane rings, respectively (the structure of CB*[6] is shown). The remarkable solubility of the new CB[*n*] derivatives in water and organic solvents allows not only their unusual binding properties toward metal and organic ions in neutral water but also their applications in ion-selective electrodes to be studied.



*Angew. Chem.* **2001**, *113*, 4363–4365

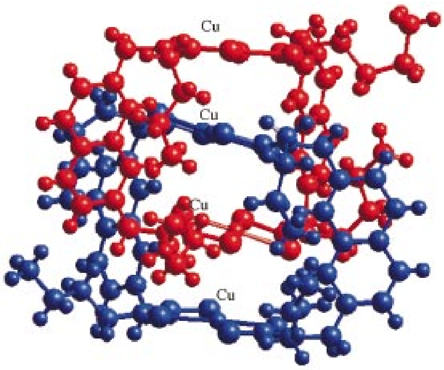
J. Zhao, H.-J. Kim, J. Oh, S.-Y. Kim,
J. W. Lee, S. Sakamoto, K. Yamaguchi,
K. Kim* .................. 4233–4235

Cucurbit[*n*]uril Derivatives Soluble in Water and Organic Solvents

**Keywords:** cucurbituril • host–guest systems • ion-selective electrodes • molecular recognition • supramolecular chemistry

**Chemical oxidation** of two preformed dinuclear copper(II) dithiocarbamate macrocycles leads to the formation of a novel mixed-valence tetranuclear copper(II)/copper(III) dithiocarbamate [2]catenane in near quantitative yield. Structural (see X-ray crystal structure), magnetic susceptibility, electrospray mass spectrometry, and electrochemical studies all support the formation of a $\mathrm{Cu^{II}Cu^{III}Cu^{II}Cu^{III}}$ tetranuclear catenane dication.

*Angew. Chem.* **2001**, *113*, 4365–4369

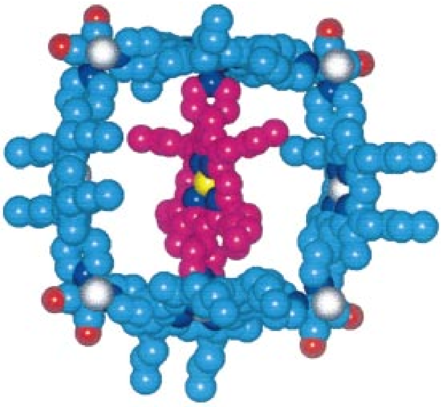


**Keywords:** catenanes · copper · mixed-valent compounds · redox chemistry · self-assembly

---

**Supramolecular complex formation** imparts stability and substrate selectivity to a simple manganese-porphyrin-based epoxidation catalyst. Lewis acid/Lewis base directed assembly was used to encapsulate the epoxidation catalyst within a supramolecular square structure to form an enzyme-like catalyst system. The "molecular square" (see picture) takes on the functions of the protein superstructure in an enzyme: it spatially protects the catalytic core from decomposition and induces reaction selectivity.

*Angew. Chem.* **2001**, *113*, 4369–4372

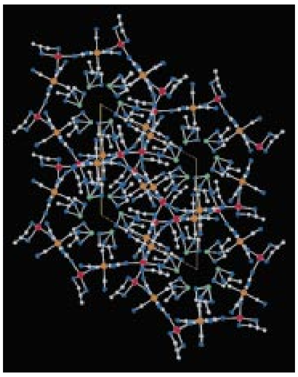


**Keywords:** epoxidation · homogeneous catalysis · host–guest systems · self-assembly · supramolecular chemistry

---

**The transparent, double bridged-(*R*)-spiral** three-dimensional polymeric complex $K_{0.4}[Cr(CN)_6]$-$[Mn(S)\text{-pn}](S)\text{-pnH}_{0.6}$ ($(S)$-pn = $(S)$-1,2-diaminopropane) has been synthesized and characterized (see X-ray structure; Cr: brown, Mn: red, C: gray, N: blue, K: green). Magnetic measurements on the complex show that the $Mn^{II}$ and $Cr^{III}$ ions interact ferrimagnetically and magnetic transition occurs at 53 K (Curie temperature).

*Angew. Chem.* **2001**, *113*, 4372–4375

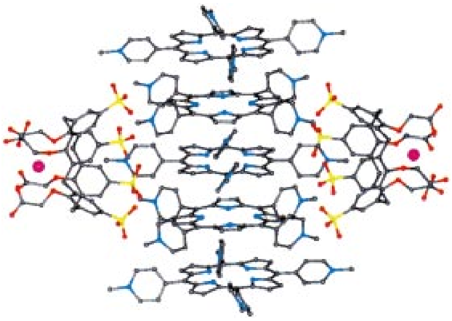


**Keywords:** chirality · chromium · helical structures · magnetic properties · manganese

---

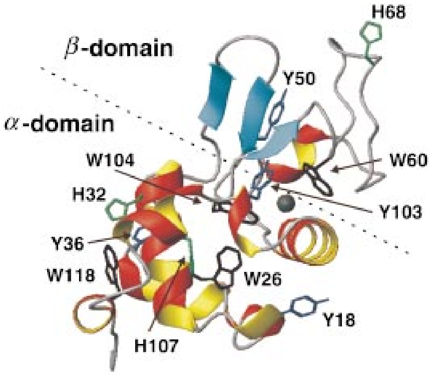
**Self-aggregation of water-soluble pyridinium-substituted porphyrins** with functionalized calixarenes leads to well-defined pH-tunable stoichiometries. Two assemblies with different porphyrin:calixarene ratios that crystallized at pH 2 and 6 (see structure) have been structurally characterized. The Job plots of Soret band broadenings indicate that these structures are also preserved in solution.

*Angew. Chem.* **2001**, *113*, 4375–4377



**Keywords:** calixarenes · host–guest systems · porphyrinoids · self-assembly · supramolecular chemistry

**Aspects of the structure of the intermediate** populated after 200 ms in the $Ca^{2+}$-induced refolding of α-lactalbumin have been derived by time-resolved photo-CIDNP NMR methods. Refolding at constant denaturant concentration was initiated by laser-induced ion release from photolabile chelators. The NMR data demonstrated that part of the polypeptide chain in the β-domain of α-lactalbumin samples adopt non-native conformations while a hydrophobic core of the α-domain is already formed (see picture).



*Angew. Chem.* **2001**, *113*, 4378–4381

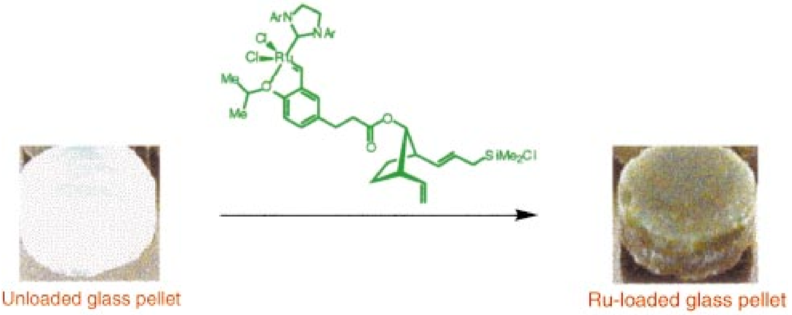
J. Wirmer, T. Kühn,
H. Schwalbe* .............. 4248–4251

Millisecond Time Resolved Photo-CIDNP NMR Reveals a Non-Native Folding Intermediate on the Ion-Induced Refolding Pathway of Bovine α-Lactalbumin

**Keywords:** calcium · NMR spectroscopy · protein folding · structure elucidation

---

**Glass-bound Ru-based catalysts!** Ru-containing glass pellets (see picture) efficiently promote olefin metathesis reactions and are easily employed in syntheses of compound libraries. These robust catalysts are active in air and commercially available solvents, can be recycled up to 16 times, and removed from reaction mixtures with a simple pair of tweezers (minimal solvent waste).



*Angew. Chem.* **2001**, *113*, 4381–4386

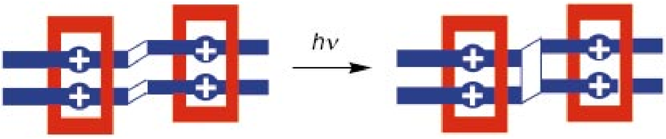
J. S. Kingsbury, S. B. Garber, J. M. Giftos,
B. L. Gray, M. M. Okamoto,
R. A. Farrer, J. T. Fourkas,*
A. H. Hoveyda* ........... 4251–4256

Immobilization of Olefin Metathesis Catalysts on Monolithic Sol–Gel: Practical, Efficient, and Easily Recyclable Catalysts for Organic and Combinatorial Synthesis

**Keywords:** combinatorial chemistry · immobilization · metathesis · ruthenium · supported catalysts

---

**A bis(dialkylammonium ion)-substituted stilbene derivative** cocrystallizes with bisparaphenylene[34]crown-10 to form, in the solid state, a 2:2 host–guest complex wherein the stilbene double bonds are aligned with a relative geometry suitable for a stereospecific photochemical [2+2] cycloaddition. When irradiated with white light, this crystalline complex forms a single diastereoisomer of the corresponding cyclobutane derivative (see schematic presentation), the stereochemistry of which has been determined unambiguously in the solid state by X-ray crystallography to be *syn-anti-syn*.



*Angew. Chem.* **2001**, *113*, 4386–4391

D. G. Amirsakis, M. A. Garcia-Garibay,*
S. J. Rowan, J. F. Stoddart,* A. J. P. White,
D. J. Williams* ............ 4256–4261

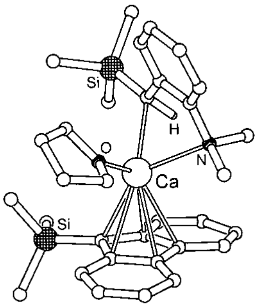
Host–Guest Chemistry Aids and Abets a Stereospecific Photodimerization in the Solid State

**Keywords:** photochemistry · pseudorotaxanes · self-assembly · solid-state reactions · template synthesis

1433-7851/01/4022-4119 $ 17.50+.50/0

**Tackling tacticity**: The first well-defined heteroleptic benzylcalcium complex (see structure) initiates the living polymerization of styrene. Chain-end control results in a polymer enriched in syndiotactic sequences. Stereo errors arise from fast inversion of the chiral carbanionic chain end. Increasing the styrene concentration accelerates the insertion and leads to a considerable reduction of the stereo errors.

*Angew. Chem.* **2001**, *113*, 4391 – 4394



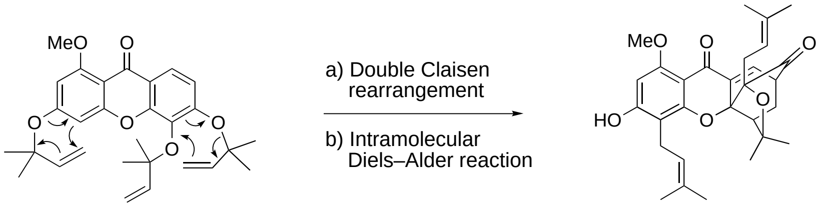
S. Harder,* F. Feil, K. Knoll 4261 – 4264

Novel Calcium Half-Sandwich Complexes for the Living and Stereoselective Polymerization of Styrene

**Keywords:** calcium · carbanions · homogeneous catalysis · polymerization · polystyrene

---

**A further demonstration of the value** of "biomimetically" inspired synthetic strategies toward natural products is provided by the title reactions that were developed for the construction of 4-oxatricyclo[4.3.1.0]decan-2-one systems from prochiral aromatic precursors. This biomimetic cascade was applied to the synthesis of 1-*O*-methylforbesione (**2**) from the prenylated xanthone **1** in one pot.



**1**

**2**: 1-*O*-methylforbesione

*Angew. Chem.* **2001**, *113*, 4394 – 4398

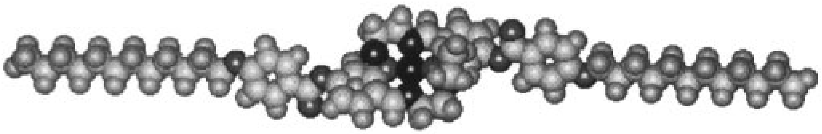
K. C. Nicolaou,* J. Li ...... 4264 – 4268

"Biomimetic" Cascade Reactions in Organic Synthesis: Construction of 4-Oxatricyclo[4.3.1.0]decan-2-one Systems and Total Synthesis of 1-*O*-Methylforbesione via Tandem Claisen Rearrangement/Diels – Alder Reactions

**Keywords:** cascade reactions · cycloaddition · natural products · rearrangement · total synthesis

---

**The rodlike $Fe^{III}$ complex** of an *N*-alkyloxysalicylidenyl-*N'*-ethyl-*N*-ethylenediamine ligand, shown as a computer model in the picture, is the first compound in which spin-crossover (SC) and liquid-crystalline (LC) properties coexist. This synergy should allow the magnetic and optical properties of SC compounds to be combined with the sensitivity of the LC state to electromagnetic fields.



*Angew. Chem.* **2001**, *113*, 4399 – 4401

Y. Galyametdinov,* V. Ksenofontov, A. Prosvirin, I. Ovchinnikov, G. Ivanova, P. Gütlich,* W. Haase ...... 4269 – 4271

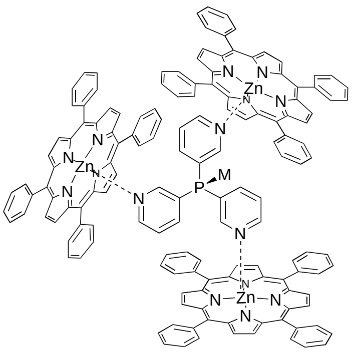
First Example of Coexistence of Thermal Spin Transition and Liquid-Crystal Properties

**Keywords:** iron · liquid crystals · metallomesogens · spin crossover

---

**Enforced ligand dissociation** as a result of steric interactions between $Zn^{II}$ porphyrin units and the N atoms of pyridylphosphane ligands determines the catalytic properties of the encapsulated transition metal complexes (see picture). These assemblies show increased catalytic activity in the palladium-catalyzed Heck reaction and rhodium-catalyzed hydroformylation. M = transition metal catalyst.

*Angew. Chem.* **2001**, *113*, 4401 – 4404

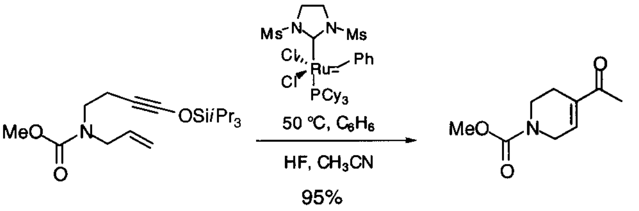


V. F. Slagt, J. N. H. Reek,* P. C. J. Kamer, P. W. N. M. van Leeuwen .... 4271 – 4274

Assembly of Encapsulated Transition Metal Catalysts

**Keywords:** homogeneous catalysis · porphyrinoids · self-assembly · supramolecular chemistry

**Mechanistically intriguing participation** of siloxyalkynes occurs in the intramolecular Ru-catalyzed metathesis with terminal alkenes (see scheme; Ms = methanesulfonyl). Combined with efficient protodesilylation, this process resulted in the development of a new method for the synthesis of highly functionalized enones starting from readily accessible acyclic precursors. Heterocyclic and polycyclic compounds were prepared efficiently, which illustrates the generality of this novel method.



*Angew. Chem.* **2001**, *113*, 4404–4407

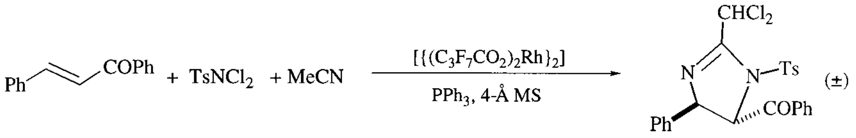
M. P. Schramm, D. S. Reddy,
S. A. Kozmin* ............ 4274–4277

Siloxyalkyne–Alkene Metathesis: Rapid Access to Highly Functionalized Enones

**Keywords:** enones • homogeneous catalysis • metathesis • siloxyalkynes • synthetic methods

---

**A three-component electrophilic reaction** transforms olefins into imidazoline and diamine derivatives (see scheme). Rhodium(II) heptafluorobutyrate dimer (2 mol%) was utilized as the catalyst and *N*,*N*-dichloro-*p*-toluenesulfonamide (TsNCl$_2$) and acetonitrile as the nitrogen sources. Modest to good yields (45–82%) and high regio- and stereoselectivity were achieved.



(66 %, stereoselectivity = 26 : 1
regioselectivity > 95 : 1)

*Angew. Chem.* **2001**, *113*, 4407–4410

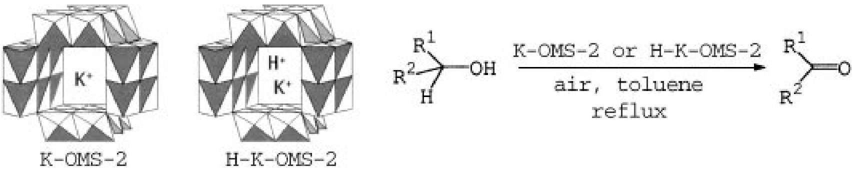
G. Li,* H.-X. Wei, S. H. Kim,
M. D. Carducci ........... 4277–4280

A Novel Electrophilic Diamination Reaction of Alkenes

**Keywords:** amination • electrophilic additions • homogeneous catalysis • nitrogen heterocycles • rhodium

---

**Mixed-valent manganese** octahedral molecular sieves K-OMS-2 and H-K-OMS-2 are used to oxidize a wide range of alcohols with 100% selectivity and 90–100% conversion in most cases. The reaction (see scheme) is aerobic, catalytic, mild, efficient, stable, inexpensive, selective, and environmentally friendly.



*Angew. Chem.* **2001**, *113*, 4410–4413

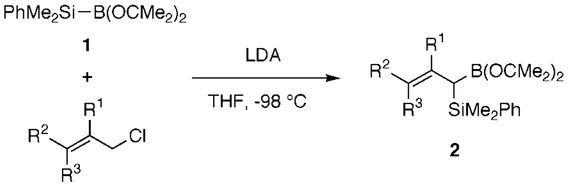
Y.-C. Son, V. D. Makwana, A. R. Howell,
S. L. Suib* ............... 4280–4283

Efficient, Catalytic, Aerobic Oxidation of Alcohols with Octahedral Molecular Sieves

**Keywords:** alcohols • heterogeneous catalysis • manganese • mixed-valent compounds • oxidation

---

**Silylboryl reagents for organic synthesis**: 1-silyl-1-boryl-2-alkenes (**2**) were prepared efficiently by *gem*-silylborylation of $\alpha$-chloroallyllithium compounds from (dimethylphenylsilyl)(pinacolato)borane (**1**; see scheme, LDA = lithium diisopropylamide) and were demonstrated to allylate acetals and aldehydes in the presence of a Lewis acid to produce (*E*)-4-alkoxy-alkenylboronates. Heating the reagents with aldehydes in the absence of Lewis acid afforded (*Z*)-4-hydroxy-alkenylsilanes stereospecifically.



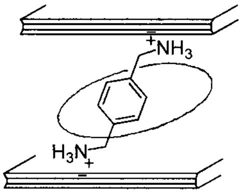
*Angew. Chem.* **2001**, *113*, 4413–4416

M. Shimizu,* H. Kitagawa, T. Kurahashi,
T. Hiyama* .............. 4283–4286

1-Silyl-1-boryl-2-alkenes: Reagents for Stereodivergent Allylation Leading to 4-Oxy-(*E*)-1-alkenylboronates and 4-Oxy-(*Z*)-1-alkenylsilanes

**Keywords:** alkenes • allylation • boron • carbenoids • silicon

**As an alternative to the rotaxane method**, an organoclay can be used as a template for the efficient formation of macrocycles (ring in schematic representation) which are easily extracted from the clay interlayer space. The four-step synthesis involved preparation of a pillared clay from the dihydrochloride salt of *p*-xylylenediamine, insertion of neutral *p*-xylylenediamine into the pillared structure, reaction of the neutral *p*-xylylenediamine in the layers with isophthaloyl chloride and formation of the tetramide macrocycle, and extraction of the product from the clay.



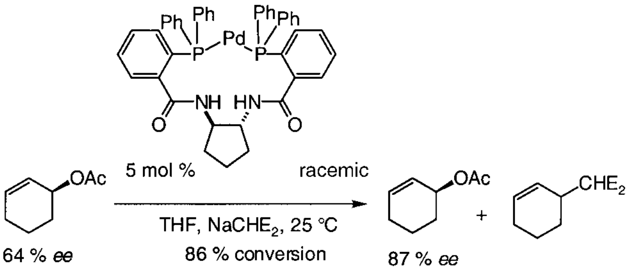
V. Georgakilas, D. Gournis,
D. Petridis* ................ 4286–4288

Organoclay Derivatives in the Synthesis of Macrocycles

Angew. Chem. **2001**, *113*, 4416–4418

**Keywords:** clays · macrocycles · supramolecular chemistry · template synthesis · through-bond interactions

**An even-handed approach**: by use of an enantiomerically enriched substrate and study of the changes in enantiomer ratio of substrate under pseudo zero-order conditions, racemic catalysts may be employed to determine whether the enantiomerically pure catalyst would be effective for kinetic resolution of the racemic substrate (see scheme; E = $CO_2Me$).



B. Dominguez, N. S. Hodnett,
G. C. Lloyd-Jones* ........ 4289–4291

Testing Racemic Chiral Catalysts for Kinetic Resolution Potential

Angew. Chem. **2001**, *113*, 4419–4421

**Keywords:** allylation · asymmetric catalysis · kinetic resolution · palladium

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

* Author to whom correspondence should be addressed

The cover picture was designed by Erik Zuidema and Vincent Slagt.

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Switch to new horizons

B. L. Feringa, (Ed.) University of Groningen, The Netherlands
Molecular Switches
2001. XVI, 464 pages. Hardcover.
DM 268.00 / £ 85.00
ISBN 3-527-29965-3

Every day we use switches to turn electric appliances on and off and no computer could function without them. Molecular switches work in the same way, changing from state one to another depending on environmental influences. However, as opposed to normal switches, molecular switches are extremely tiny and their application in nanotechnology, biomedicine and computer chip design opens up whole new horizons.

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- Fulgide based photoswitches
- Azulenes
- Electrooptical switches
- Electron transfer photoswitching
- Metallo-based photoswitches
- Photoswitches of liquid crystals
- Photoresponsive polymers, monolayers and thin films
- Supramolecular switches
- Metallo-rotaxanes and catenanes
- Supramolecular switches;
- Molecular shuttles
- Switchable molecular receptors and recognition processes
- Biomolecular switches.

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