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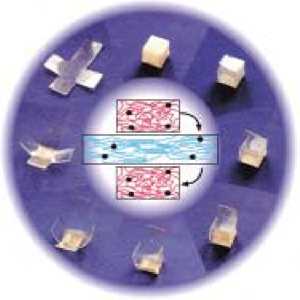
COVER PICTURE

The cover picture shows the thermally induced shape-memory effect for a covalently cross-linked polymer network. The polymer in its temporary shape (cube, picture on top) is heated from room temperature up to 70°C. Within 60 seconds the sample recovers its memorized, permanent shape of a nearly planar foil (picture on top left). The visual change of the material from opaque to transparent is caused by the melting of crystallites of the switching segments. The scheme in the center of the picture illustrates the molecular mechanism of the shape-memory effect. The shown polymer network, which is synthesized from poly(ε-caprolactone)dimethacrylate as macromonomer, is one of the first polymer systems that have specifically been developed for applications in the biomedical field. The net points (black) determine the permanent shape while the crystallites (blue) stabilize the temporary shape. More on the current state and the potential of this technology can be found in the review by A. Lendlein and S. Kelch on p. 2034 ff.

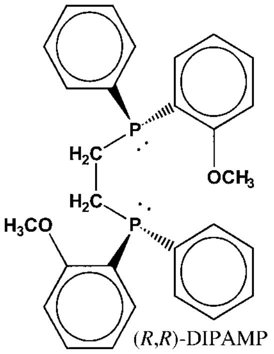


REVIEWS

Contents

Phosphorus is where the action is! Knowles and his co-workers were convinced that only chiral phosphorus ligands such as (*R*,*R*)-DIPAMP (see picture), whose stereogenic center lies directly on the phosphorus atom, would lead to high enantiomeric excesses when used as catalysts in asymmetric hydrogenation reactions. This hypothesis was contradicted by the development of ligands with chiral carbon backbones, and the mystery of how the phosphorus ligands work must still be solved.

Angew. Chem. **2002**, *114*, 2096–2107

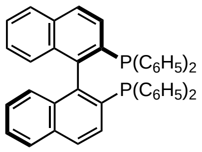


(*R*,*R*)-DIPAMP

Keywords: asymmetric catalysis · asymmetric hydrogenation · Nobel lecture · phosphane ligands · rhodium

From sub-femtomole to ton scale: Asymmetric catalysis with organometallic complexes plays a major role in all areas of modern synthetic chemistry. The author has worked in this area since the beginning and has been honored for his research with the Nobel prize. Asymmetric hydrogenation with transition-metal complexes of BINAP ligands (see picture) has been an important step in his personal research career.

Angew. Chem. **2002**, *114*, 2108–2123



(*R*)-BINAP

R. Noyori* 2008–2022

Asymmetric Catalysis: Science and Opportunities (Nobel Lecture)

Keywords: asymmetric catalysis · asymmetric hydrogenation · Nobel lecture · phosphane ligands · ruthenium

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Fishing for coelacanths (see picture) is how the author regards his Nobel-prize-winning research on the selective, asymmetric oxidation of alkenes. His procedures for asymmetric epoxidation and dihydroxylation use small, highly selective catalysts that are tolerant of a wide range of substrates.

Angew. Chem. **2002**, *114*, 2126–2135

K. B. Sharpless* 2024–2032

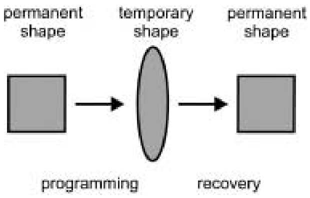
Searching for New Reactivity (Nobel Lecture)

Keywords: asymmetric catalysis · epoxidation · hydroxylation · Nobel lecture · N ligands

---

Upon exposure to an external stimulus, shape-memory polymers can change their shape (see scheme). This ability opens up numerous fields of application, such as intelligent, bulky implants, which can be inserted in a compressed, temporary shape into the body through a small incision, or auto bodies, which could be brought back to their original shape after a collision by a simple heat treatment. The current state and the potential of this technology is summarized in the article.

Angew. Chem. **2002**, *114*, 2138–2162



A. Lendlein,* S. Kelch 2034–2057

Shape-Memory Polymers

Keywords: block copolymers · elastomers · materials science · polymers · shape-memory polymers

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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.org

Poly(*p*-phenylenephosphaalkene): A π-Conjugated Macromolecule Containing P=C Bonds in the Main Chain	V. A. Wright, D. P. Gates*	◆
Catalytic Activity and Poisoning of Specific Sites on Supported Metal Nanoparticles	S. Schauermann, J. Hoffmann, V. Johánek, J. Hartmann, J. Libuda,* H.-J. Freund	
Understanding Zeolite Catalysis: Inverse Shape Selectivity Revised	M. Schenk, S. Calero, T. L. M. Maesen, L. L. van Benthem, M. G. Verbeek, B. Smit*	
Highly Selective Transport of Organic Compounds by Using Supported Liquid Membranes Based on Ionic Liquids	L. C. Branco, J. G. Crespo, C. A. M. Afonso*	
Atom-Transfer Tandem Radical Cyclization Reactions Promoted by Lewis Acids	D. Yang,* S. Gu, H.-W. Zhao, N.-Y. Zhu	

1433-7851/02/4112-1977 $ 20.00+.50/0

ESSAY

Uncle Tungsten. Memories. In the new book by Oliver Sacks the history of chemistry, encompassing the ancient and the modern subdisciplines, is captured and told retrospectively through the eyes, heart, and voice of a passionate and precocious teenager.

Angew. Chem. **2002**, *114*, 2163 – 2170

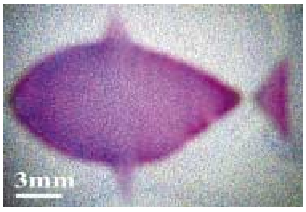
J. M. Thomas* .... 2059 – 2065

An Omnivorous Curiosity, a Sense of Wonder, and a Taste for the Spectacular

Keywords: Sacks, Oliver • history of chemistry

COMMUNICATIONS

The unique photochemical properties of TiO_2 provides a stepwise approach for the easy and precise patterning of colloidal crystal films. In this approach patterns of hydrophobic and hydrophilic areas are formed on a TiO_2 surface and then a colored film of monodispersed polystyrene spheres is deposited on to the hydrophilic region (fish-shaped pattern in the example shown).



Angew. Chem. **2002**, *114*, 2171 – 2174

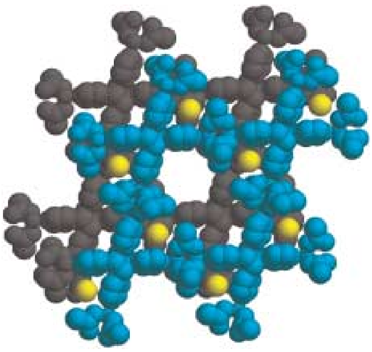
Z.-Z. Gu, A. Fujishima,
O. Sato* .... 2067 – 2070

Patterning of a Colloidal Crystal Film on a Modified Hydrophilic and Hydrophobic Surface

Keywords: colloids • surface chemistry • thin films • titanium dioxide • wettability

---

Gridlock: A porous metal – organic framework with an interior tailored supramolecularly with organic groups is described (see structure; two grids have been differentiated using cyan and gray, while the yellow spheres represent included methyl groups). The approach relies on inverting the role of a secondary building unit (SBU) and an organic linker such that the organic linker serves as a node and the SBU serves as a linear bridge. The organic node used to construct the framework has been obtained by way of a template-directed solid-state organic synthesis.



Angew. Chem. **2002**, *114*, 2174 – 2177

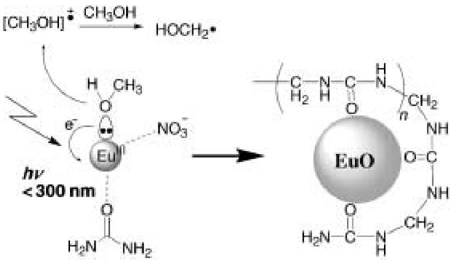
G. S. Papaefstathiou,
L. R. MacGillivray* .... 2070 – 2073

An Inverted Metal-Organic Framework with Compartmentalized Cavities Constructed by Using an Organic Bridging Unit Derived from the Solid State

Keywords: copper • cycloaddition • host – guest systems • layered compounds • self-assembly

---

Photoinduced enhancement of magnetization is exhibited by polyurea-modified EuO nanocrystals, prepared by photolysis of europium(III) nitrate and urea in methanol (see scheme). The nanoparticles, which have an average diameter of 3.4 nm and a narrow size distribution, also exhibit a remarkably high emission quantum yield.



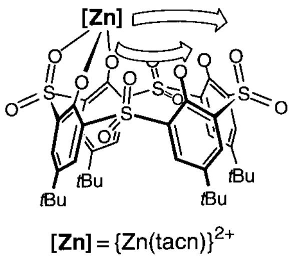
Angew. Chem. **2002**, *114*, 2177 – 2179

Y. Hasegawa, S. Thongchant, Y. Wada, H. Tanaka, T. Kawai, T. Sakata, H. Mori, S. Yanagida* .... 2073 – 2075

Enhanced Luminescence and Photomagnetic Properties of Surface-Modified EuO Nanocrystals

Keywords: lanthanides • luminescence • magnetic properties • nanostructures

The Zn^{II} ion slides smoothly over an "O_8" surface on the NMR spectroscopic timescale. The surface is formed by two phenol oxygen atoms, two phenoxy oxygen atoms, and four sulfonyl oxygen atoms of an analogue of *p-tert*-butylcalix[4]arene in a cone conformation in which the bridging methylene groups are replaced by sulfonyl moieties (see scheme). tacn = 1,4,7-triazacyclononane.



Angew. Chem. **2002**, *114*, 2180–2182

T. Kajiwara,* S. Yokozawa, T. Ito,* N. Iki, N. Morohashi, S. Miyano* .. 2076–2078

Zinc(II) Slides on a Ligand Surface: The X-Ray Crystal Structure and Dynamic Behavior in Solution of [Zn(H_2L)(tacn)]

Keywords: calixarenes • fluxionality • macrocyclic ligands • solid-state structures • zinc

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Short bonds explained at long last: The charge-density distribution in the S–N bonds of $H_2C\{S(NtBu)_2(NHtBu)\}_2$, the NR analogue of methane disulfonic acid $H_2C\{S(O)_2(OH)\}_2$, was studied by high-resolution X-ray diffraction and subsequent multipole structure refinement (see picture). This experiment reveals that all three nitrogen atoms at each sulfur atom are sp^3 hybridized. The formal S–N double bonds are shortened by electrostatic reinforcement and not by $p_\pi - d_\pi$ interaction.

Angew. Chem. **2002**, *114*, 2183–2186

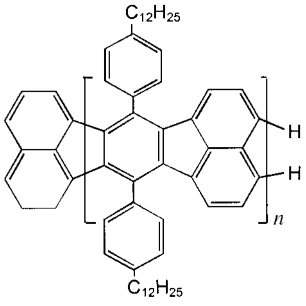
D. Leusser, B. Walfort, D. Stalke* 2079–2082

Charge-Density Study of Methane Di(triimido)sulfonic Acid $H_2C\{S(NtBu)_2(NHtBu)\}_2$—the NR Analogue of $H_2C\{S(O)_2(OH)\}_2$

Keywords: bond theory • electron-density distribution • nitrogen • structure elucidation • sulfur

---

Chain length and dimerization, the missing link? The influence of chain length on the dimerization of the extended π-conjugated ladder-type fluoranthenopyracylene oligomers (see picture) during charge transfer is studied by cyclic voltammetry and in situ ESR/UV/Vis-NIR spectroelectrochemistry. The π conjugation in higher extended structures is found to be sufficient for the stabilization of charges in the molecule and disfavors chemical dimerization. This finding is an indication that dimerization in organic conducting polymers may not be a necessary stabilization mechanism of general validity.



Angew. Chem. **2002**, *114*, 2187–2190

L. Dunsch,* P. Rapta, N. Schulte, A. D. Schlüter 2082–2086

Structural Dependence of Redox-Induced Dimerization as Studied by In Situ ESR/UV/Vis-NIR Spectroelectrochemistry: The Fluoranthenopyracylene Oligomers

Keywords: conducting materials • conducting polymers • cyclic voltammetry • EPR spectroscopy • spectroelectrochemistry

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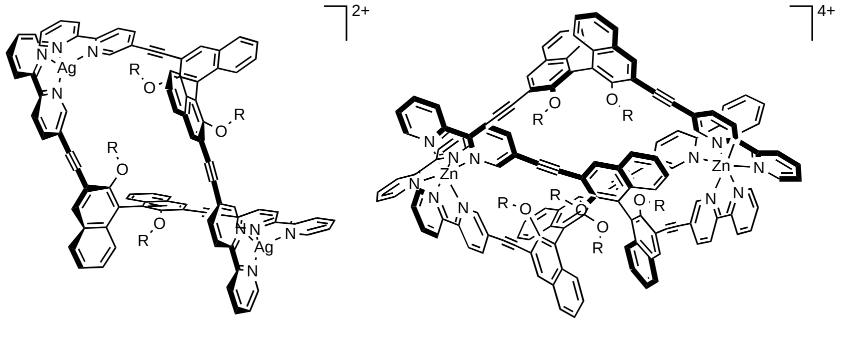
Chiral cavities with inward-pointing functional groups are afforded by chiral bis(bipyridine) ligands. Upon coordination to suitable transition-metal ions, these self-assemble in a diastereoselective manner to form double- and triple-stranded helicates (left and right pictures, respectively).



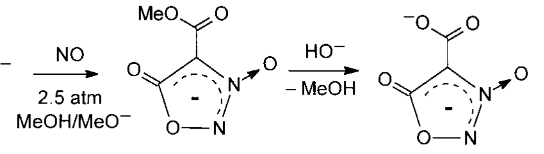
Angew. Chem. **2002**, *114*, 2190–2194

A. Lützen,* M. Hapke, J. Griep-Raming, D. Haase, W. Saak 2086–2089

Synthesis and Stereoselective Self-Assembly of Double- and Triple-Stranded Helicates

Keywords: coordination chemistry • diastereoselectivity • helical structures • N ligands • supramolecular chemistry

An unusual heterocycle results from the Traube reaction of dimethyl malonate and nitric oxide (see scheme). This newly characterized *E*-ONNO sydnone is formed preferentially to the condensation product with a *Z* geometry.



Traube's "oxazomalonic" acid

Angew. Chem. **2002**, *114*, 2200–2203

N. Arulsamy, D. S. Bohle* 2089–2091

Traube's "Oxazomalonic Acid" is a 3-Hydroxysydnone Carboxylate with an *E*-ONNO Geometry

Keywords: condensations · nitrogen heterocycles · nitrogen oxides · reaction mechanisms · structure elucidation

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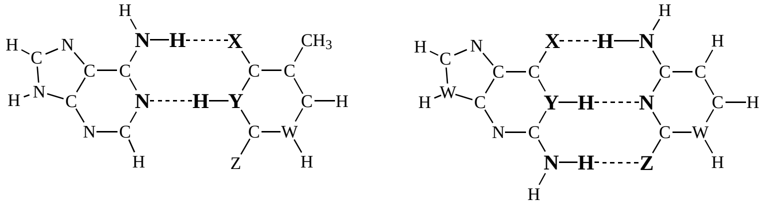
Not only the shape of the bases, but also the orbital interactions in the hydrogen bonds are essential for DNA replication, as follows from quantum-chemical analyses of Watson–Crick pairs and mimics thereof (see Figure: X, Z = O, F, H; W, Y = N, C), in combination with earlier experimental results.



A $T_{XY'Z}$ $G_{XY'N'}$ $C_{N'NZ}$

Angew. Chem. **2002**, *114*, 2194–2197

C. Fonseca Guerra, F. M. Bickelhaupt* 2092–2095

Orbital Interactions in Strong and Weak Hydrogen Bonds are Essential for DNA Replication

Keywords: charge transfer · density functional calculations · DNA replication · hydrogen bonds · orbital interactions

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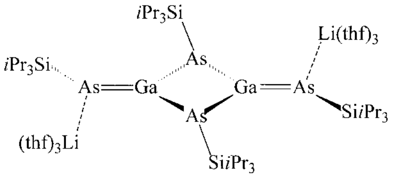
A planar Ga_2As_4 unit is the central structural motive of the title compound (see picture). The compound results from the reaction of $GaCl_3$ with $Li_2AsSi\textit{i}Pr_3$ in a mixture of THF and heptane. It is the first example of a molecule with Ga–As double bonds.



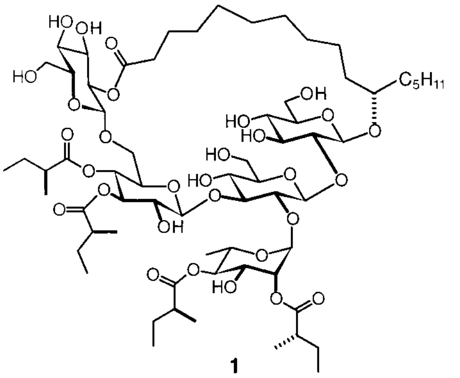
Angew. Chem. **2002**, *114*, 2198–2200

C. von Hänisch,* O. Hampe 2095–2097

$[\{Li(thf)_3\}_2Ga_2\{As(Si\textit{i}Pr_3)\}_4]$—A Compound with Gallium–Arsenic Double Bonds

Keywords: arsenic · gallium · multiple bonds · Zintl anions

The reliability of ring-closing metathesis, even in complex cases, is highlighted in the first total synthesis of the structurally intriguing resin glycoside woodrosin I (**1**). The synthesis also shows the maturity of the trichloroacetimidate method for glycosylation and features the most advanced application of an orthoester rearrangement for the formation of a *β*-glycosidic bond.



1

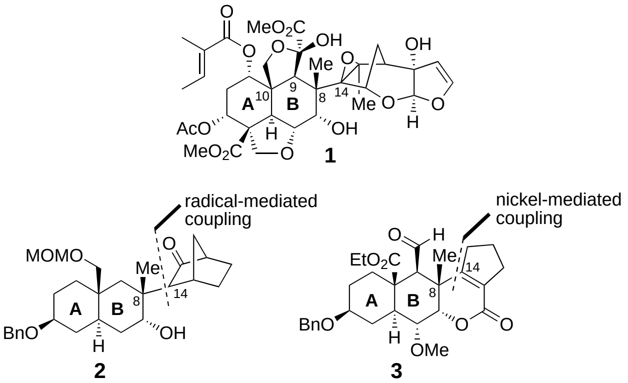
Angew. Chem. **2002**, *114*, 2203–2206

A. Fürstner,* F. Jeanjean, P. Razon 2097–2101

Total Synthesis of Woodrosin I

Keywords: glycosides · macrocycles · metathesis · natural products · ruthenium

Two strategies—one goal: Two novel methodologies for the construction of the crowded C^8–C^{14} bond of azadirachtin (**1**) are described. The first approach to this thorny synthetic hurdle utilizes radical chemistry and furnishes model system **2**, whereas the second foray employs a nickel-mediated coupling reaction and affords model system **3**.



Angew. Chem. **2002**, *114*, 2207–2210

Angew. Chem. **2002**, *114*, 2211–2214

K. C. Nicolaou,* M. Follmann,
A. J. Roecker, K. W. Hunt 2103–2106

Model Studies Towards Azadirachtin: Part 1. Construction of the Crowded C8–C14 Bond by Radical Chemistry

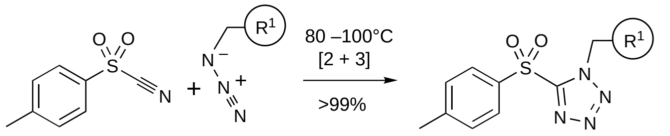
K. C. Nicolaou,* A. J. Roecker,
M. Follmann, R. Baati …… 2107–2110

Model Studies Towards Azadirachtin: Part 2. Construction of the Crowded C8–C14 Bond by Transition Metal Chemistry

Keywords: azadirachtin · cascade reactions · natural products · radical reactions · steric hindrance

---

Quantitative yields are observed from the reaction of aryl sulfonyl cyanides with unhindered azides by simply heating at 80–100°C (see scheme). The reactions are run neat, and there are no by-products, so no workup is necessary. The resulting tetrazoles are activated for rapid functionalization by an S_NAr reaction.



Angew. Chem. **2002**, *114*, 2214–2217

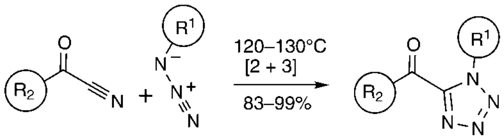
Z. P. Demko,
K. B. Sharpless* ………… 2110–2113

A Click Chemistry Approach to Tetrazoles by Huisgen 1,3-Dipolar Cycloaddition: Synthesis of 5-Sulfonyl Tetrazoles from Azides and Sulfonyl Cyanides

Keywords: azides · cyanides · cycloaddition · nitrogen heterocycles · synthetic methods

---

Click chemistry: Acyl cyanides react with alkyl azides in high yield by heating at 120–130°C (see scheme). The reactions are run neat, and the workup is simple. When *p*-nitrophenyl cyanoformate is used as the dipolarophile, the resulting tetrazoles are activated for rapid functionalization as an activated ester.



Angew. Chem. **2002**, *114*, 2217–2220

Z. P. Demko,
K. B. Sharpless* ………… 2113–2116

A Click Chemistry Approach to Tetrazoles by Huisgen 1,3-Dipolar Cycloaddition: Synthesis of 5-Acyltetrazoles from Azides and Acyl Cyanides

Keywords: azides · cyanides · cycloaddition · nitrogen heterocycles · synthetic methods

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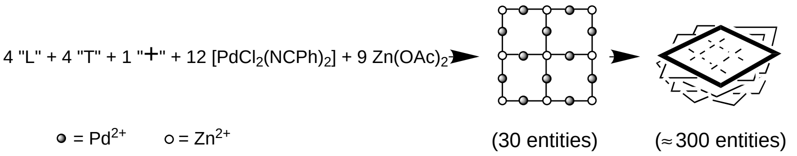
Piles of molecules: Self-assembled nonamer arrays self-organize into 3D aggregates (see scheme: L = "L-shaped" porphyrin (corner piece), T = "T-shaped" porphyrin (side piece), + = "cross-shaped" porphyrin (center)). The size of the nanoscaled material on surfaces can be controlled from 1 nonamer to 50-nm-tall aggregates by chemistry, kinetics, and choice of surface.



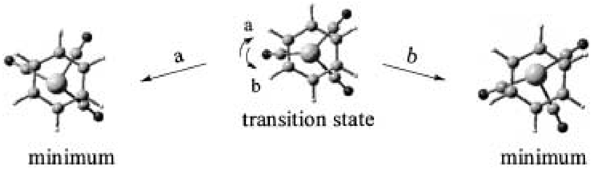
Angew. Chem. **2002**, *114*, 2221–2223

T. N. Milic, N. Chi, D. G. Yablon,
G. W. Flynn, J. D. Batteas,*
C. M. Drain* …………… 2117–2119

Controlled Hierarchical Self-Assembly and Deposition of Nanoscale Photonic Materials

Keywords: nanostructures · palladium · porphyrinoids · self-assembly · zinc

Two of each! In the C_{3v} point group, the 16-electron $[\eta^6\text{-(benzene)Nb(CO)}_3]^+$ fragment has accessible Jahn–Teller-active singlet and triplet electronic states. Distortion into the C_s point group leads to two low-energy minima and two transition states (see scheme). This finding is shown to have important implications for other unsaturated complexes such as $[\eta^5\text{-CpMo(CO)}_2\text{Cl}]$ and $[\eta^5\text{-CpMn(CO)}_2]$ (Cp = cyclopentadienyl).



Angew. Chem. **2002**, *114*, 2224–2226

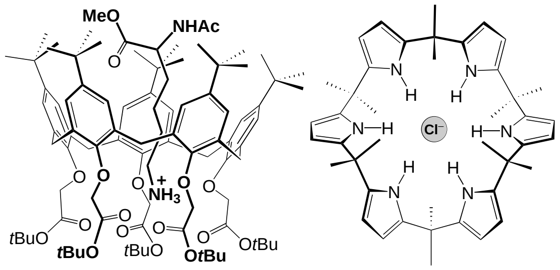
F. Abu-Hasanayn,* P. H.-Y. Cheong,
M. Oliff 2120–2122

Identification of Jahn–Teller Effects in both Singlet and Triplet Low-Energy States of $[(\eta^6\text{-benzene})\text{Nb(CO)}_3]^+$

Keywords: density functional calculations · electron-deficient compounds · Jahn–Teller distortion · transition metals

---

Confinement of the charged constituents of ion-paired organic salts within the complementary cavities of suitably chosen pairs of cation and anion receptors to form supramolecular systems, as shown for the complexation of N^α-Ac-L-Lys-OMe · HCl by a calix[5]arene/calix[6]pyrrole combination, results in a remarkable (up to 10^4-fold) enhancement of the binding ability of the binary host systems compared to that of either receptor taken individually.



Angew. Chem. **2002**, *114*, 2226–2230

G. Cafeo, G. Gattuso, F. H. Kohnke,
A. Notti, S. Occhipinti, S. Pappalardo,
M. F. Parisi* 2122–2126

Remarkable Boosting of the Binding of Ion-Paired Organic Salts by Binary Host Systems

Keywords: calixarenes · calixpyrroles · cooperative effects · inclusion compounds · ion-pair recognition

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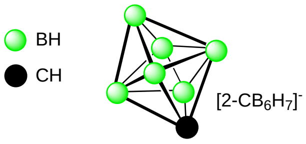
Opening up *closo*-cluster chemistry: The first representative of the seven-vertex *closo* monocarbaborane series, the $[closo\text{-2-CB}_6\text{H}_7]^-$ ion (see structure), was isolated together with the $[closo\text{-1-CB}_7\text{H}_8]^-$ ion from simple reactions between $nido\text{-1-CB}_8\text{H}_{12}$ and Et_3N. Both ions exhibit high stability in air and are potentially useful for weakly coordinating anion chemistry.



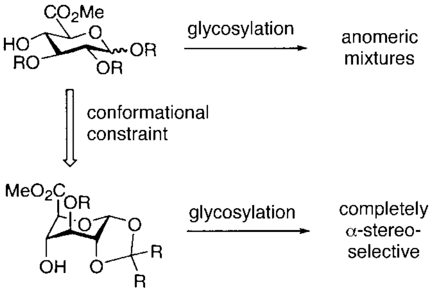
Angew. Chem. **2002**, *114*, 2230–2232

B. Štíbr,* O. L. Tok, W. Milius,
M. Bakardjiev, J. Holub, D. Hnyk,
B. Wrackmeyer 2126–2128

The $[closo\text{-2-CB}_6\text{H}_7]^-$ Ion: The First Representative of the 7-Vertex Monocarbaborane Series

Keywords: boron · carboranes · structure elucidation

Complete control over the stereoselectivity of key coupling reactions in the synthesis of heparin can be exerted by conformationally locking the uronic acid acceptor (see scheme).



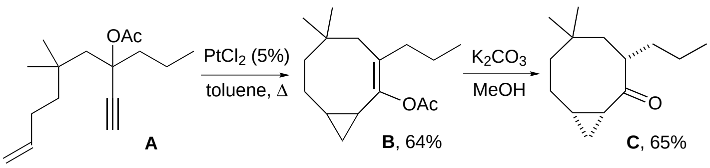
Angew. Chem. **2002**, *114*, 2232–2235

H. A. Orgueira, A. Bartolozzi, P. Schell,
P. H. Seeberger* 2128–2131

Conformational Locking of the Glycosyl Acceptor for Stereocontrol in the Key Step in the Synthesis of Heparin

Keywords: carbohydrates · conformation analysis · glycosylation · stereoselectivity

The versatile ketone C can be obtained by hydrolyzing cyclooctene **B**, which is formed in a $PtCl_2$-catalyzed cycloisomerization reaction from the enyne precursor **A**. A carbene platinum complex is invoked in the process, which also represents one of the few efficient syntheses of functionalized cyclooctanes from acyclic precursors.



Angew. Chem. **2002**, *114*, 2236–2239

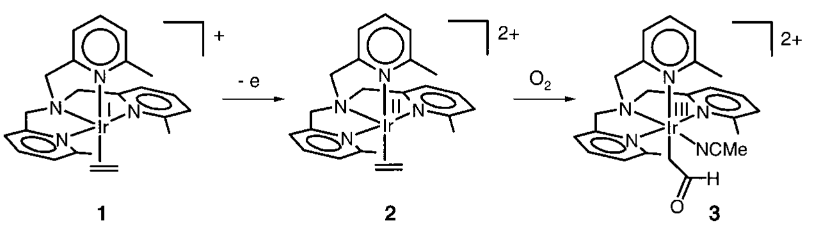
E. Mainetti, V. Mouriès, L. Fensterbank,*
M. Malacria,*
J. Marco-Contelles* 2132–2135

The Effect of a Hydroxy Protecting Group on the $PtCl_2$-Catalyzed Cyclization of Dienynes—A Novel, Efficient, and Selective Synthesis of Carbocycles

Keywords: carbenes · carbocations · diastereoselectivity · enynes · platinum

---

Oxidation induces oxygenation: The first Ir^{II}–ethene complex ever (**2**) was obtained by one-electron oxidation of the corresponding Ir^{I}–ethene complex **1**. Whereas **1** reacts with dioxygen to give an Ir^{III}–peroxo-ethene complex, the Ir^{II}–ethene complex **2** activates dioxygen towards C–O bond formation and gives the Ir^{III}–formylmethyl complex **3**.



Angew. Chem. **2002**, *114*, 2239–2242

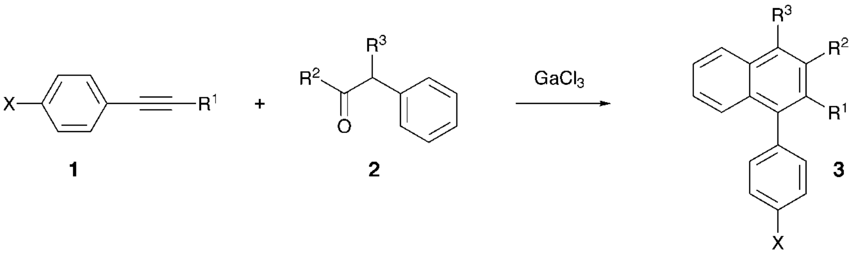
B. de Bruin,* T. P. J. Peters, S. Thewissen,
A. N. J. Blok, J. B. M. Wilting,
R. de Gelder, J. M. M. Smits,
A. W. Gal* 2135–2138

Dioxygen Activation by a Mononuclear Ir^{II}–Ethene Complex

Keywords: alkenes · iridium · N ligands · O–O activation · oxidation

---

A convenient synthesis of polysubstituted naphthalenes 3 involves the gallium trichloride catalyzed coupling of aromatic alkynes **1** and phenyl acetaldehydes or ketones **2** in dichloromethane. The reaction is highly regioselective.



Angew. Chem. **2002**, *114*, 2242–2245

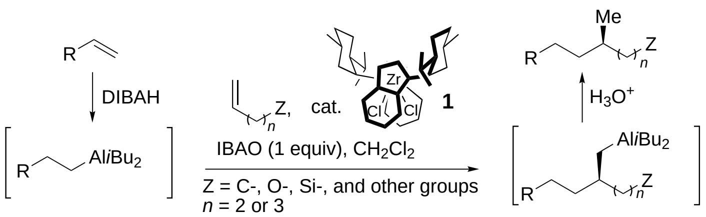
G. S. Viswanathan, M. Wang,
C.-J. Li* 2138–2141

A Highly Regioselective Synthesis of Polysubstituted Naphthalene Derivatives through Gallium Trichloride Catalyzed Alkyne–Aldehyde Coupling

Keywords: aldehydes · alkynes · gallium · naphthalenes · synthetic methods

---

Methyl-substituted alkanols have been synthesized enantioselectively (90–93% *ee*) in a one-pot hydroalumination/carboalumination tandem process (see scheme). This enantioselectively represents an increase of about 15% from the previously attainable *ee* values. DIBAH = diisobutylaluminum hydride, IBAO = isobutylaluminoxane.



Angew. Chem. **2002**, *114*, 2245–2247

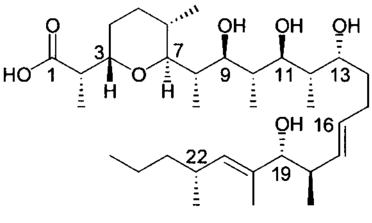
S. Huo, J.-c. Shi,
E.-i. Negishi* 2141–2143

A New Protocol for the Enantioselective Synthesis of Methyl-Substituted Alkanols and Their Derivatives through a Hydroalumination/Zirconium-Catalyzed Alkylalumination Tandem Process

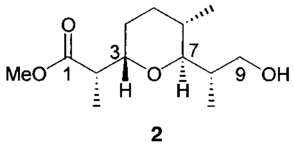
Keywords: alcohols · alkenes · aluminum · asymmetric catalysis · C–C coupling · zirconium

1433-7851/02/4112-1983 $ 20.00+.50/0

Antibiotics made from cyclopropylmethanols: The C1–C9 subunit (**2**) of zincophorin (**1**) has been synthesized by using three key steps: a hydroboration of an enantiomerically enriched isopropenylcyclopropane, an aldol reaction, and an intramolecular oxymercuration of a cyclopropylmethanol.



1



2

Angew. Chem. **2002**, *114*, 2248–2250

J. Cossy,* N. Blanchard, M. Defosseux,
C. Meyer* 2144–2146

A Synthetic Approach towards the
C1–C9 Subunit of Zincophorin

Keywords: aldol reaction · mercury · natural products · synthesis design · zincophorin

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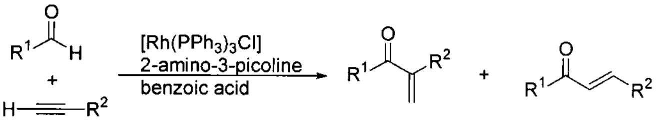
Terminal alkynes successfully undergo chelation-assisted hydroacylation with aldehydes to give branched or linear alkyl α,β-unsaturated ketones (see scheme).



Angew. Chem. **2002**, *114*, 2250–2251

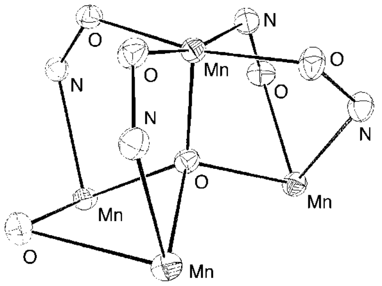
C.-H. Jun,* H. Lee, J.-B. Hong,
B.-I. Kwon 2146–2147

Efficient and Selective Hydroacylation of
1-Alkynes with Aldehydes by a
Chelation-Assisted Catalytic System

Keywords: C–H activation · homogeneous catalysis · hydroacylation · ketones · rhodium

---

A difference of two electrons: A tetranuclear cluster $[\mathrm{Mn^{II}Mn^{II}Mn^{II}Mn^{IV}(O)(pko)_4(3,4\text{-}D)_4]\cdot 2.5\,CH_3OH}$ (Hpko = di(2-pyridyl)ketonoxime, H-3,4-D = 3,4-dichlorophenoxy acetic acid) with a (μ_4-O)Mn$_4$ bridging moiety is reported (see core structure). This compound is the only example of a manganese cluster with a 2e$^-$ difference between the oxidation states of the metal ions and with four metal centers interacting through a μ_4-O bridging atom.



Angew. Chem. **2002**, *114*, 2252–2254

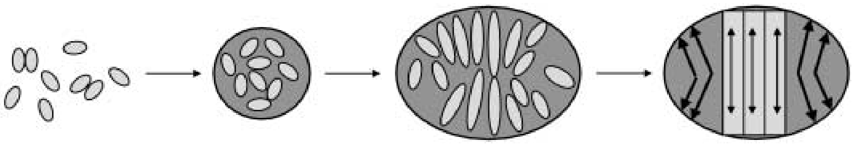
T. Afrati, C. Dendrinou-Samara,
C. P. Raptopoulou, A. Terzis,
V. Tangoulis,*
D. P. Kessissoglou* 2148–2150

A Tetranuclear Mixed-Valent Mn$^{II}_3$Mn^{IV}
Compound with a (μ_4-O)Mn$_4$ Core

Keywords: bioinorganic chemistry · manganese · metal–oxo complexes · mixed-valent compounds · N,O ligands

---

A controlled quenching process allows the nucleation period to be increased sufficiently, such that high-resolution transmission electron microscopy can be used to reveal the structural and shape transformations during the onset and development of mesophase ordering of the hexagonally ordered silica–surfactant mesophase MCM-41 (see scheme).



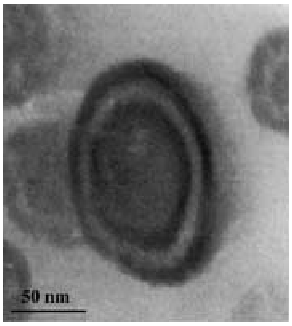
Angew. Chem. **2002**, *114*, 2255–2257

S. Sadasivan, C. E. Fowler, D. Khushalani,
S. Mann* 2151–2153

Nucleation of MCM-41 Nanoparticles by
Internal Reorganization of Disordered
and Nematic-Like Silica–Surfactant
Clusters

Keywords: mesophases · mesoporous materials · nanostructures · silica · surfactants

A three-layer substructure morphology is found in the vesicular nanostructures formed (see transmission electron micrograph) upon melt blending of polyamide 12 (PA12) with a symmetric polystyrene-*b*-polyisoprene (PS-*b*-PIP) copolymer end-capped by an anhydride group. However, macrophase separation occurs when the diblock is unreactive.



Angew. Chem. **2002**, *114*, 2258–2260

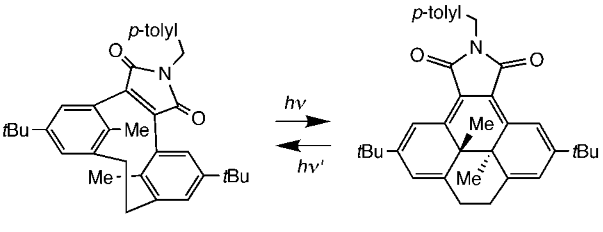
C. Koulic, Z. Yin, C. Pagnoulle,
R. Jérôme* 2154–2156

Vesicular Nanostructures Prepared by Reactive Melt Blending

Keywords: block copolymers · melt blending · nanostructures · self-assembly · vesicles

---

No racemization occurs in the first reported enantioselective photochromic reaction. Upon irradiation with UV light, a single enantiomer of [2.2]metacyclophane-1-ene **1a** undergoes photocyclization to give a single enantiomer of tetrahydropyrene **1b**. Upon irradiation with visible light, **1b** is converted back cleanly into the initial enantiomer **1a**.



1a **1b**

Angew. Chem. **2002**, *114*, 2260–2261

M. Takeshita,* T. Yamato ... 2156–2157

Enantioselective Photochromic Reaction of a [2.2]Metacyclophan-1-ene

Keywords: chiral resolution · circular dichroism · cyclophanes · enantioselectivity · photochromism

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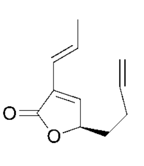
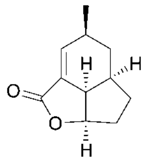
An intramolecular Diels–Alder reaction with inverse electron demand in a polyketide biosynthetic pathway is reported in which the rate of the cyclization is enhanced in vivo. Alive mycelia of the fungus *Galiella rufa* catalyze the cyclization of (−)-pregaliellalactone (**1**) to (+)-desoxygaliellalactone (**2**), while dead mycelia have no effect. No rate increase was observed with the unnatural enantiomer (+)-**1**.



1



2

Angew. Chem. **2002**, *114*, 2261–2264

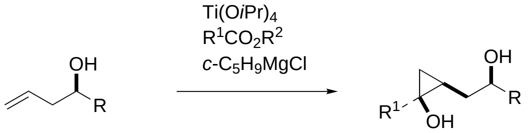
M. Johansson, B. Köpcke, H. Anke,
O. Sterner* 2158–2160

Cyclization of (−)-Pregaliellalactone in the Fungus *Galiella rufa*

Keywords: biosynthesis · cycloaddition · enzyme catalysis · natural products

---

The hydroxy group regulates the stereoselectivity in a modification of the titanium-mediated Kulinkovich cyclopropanation procedure (see scheme). This method provides a diastereoselective synthesis of *trans*-1,2-dialkylcyclopropanols, which starts with homoallylic alcohols and proceeds via a bicyclic titanacyclopropane intermediate. Enantiopure products may also be obtained if the corresponding chiral alcohols are used.



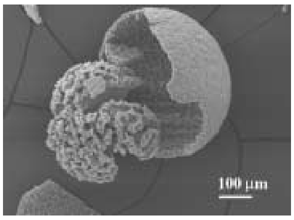
Angew. Chem. **2002**, *114*, 2264–2266

L. G. Quan, S.-H. Kim, J. C. Lee,
J. K. Cha* 2160–2162

Diastereoselective Synthesis of *trans*-1,2-Dialkylcyclopropanols by the Kulinkovich Hydroxycyclopropanation of Homoallylic Alcohols

Keywords: allylic compounds · cyclization · cyclopropanation · diastereoselectivity · titanium

Spheres without templates: The direct assembly of a complex inorganic polymer with a spherical-shell architecture (see electron microscopy image) was obtained by addition of polyacrylate or polyaspartate during the crystallization of octacalcium phosphate from aqueous solutions. The process does not require the intervention of external templates, and involves the radial growth of dense multilayered spheroids, secondary overgrowth of a porous thin-shell precursor, and anisotropic dissolution of the spheroidal cores.



Angew. Chem. **2002**, *114*, 2267 – 2270

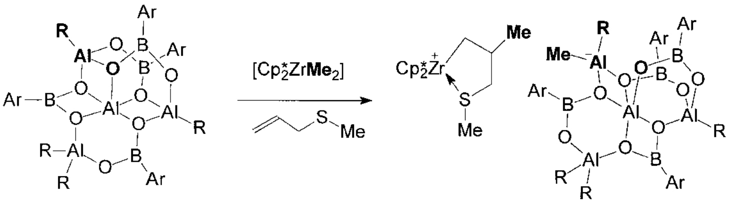
A. Bigi,* E. Boanini, D. Walsh, S. Mann .... 2163 – 2166

Morphosynthesis of Octacalcium Phosphate Hollow Microspheres by Polyelectrolyte-Mediated Crystallization

Keywords: calcium • crystal growth • materials science • microspheres • phosphates

---

How do alumoxane activators activate? Reaction (1) may help to answer this question. The product of this reaction is a zirconocene alkyl cation ($Cp^* = C_5Me_5$) with its methylated boralumoxane anion. The structure of this compound is in accord with Barron's "latent Lewis acidity" concept for alumoxane activators.



(1)

Angew. Chem. **2002**, *114*, 2270 – 2273

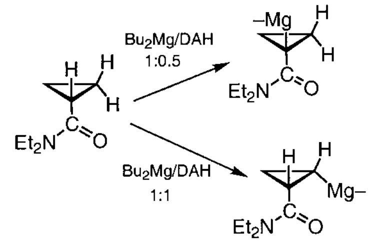
B. Richter, A. Meetsma, B. Hessen,* J. H. Teuben .... 2166 – 2169

Structural Characterization of a Cationic Zirconocene Olefin Polymerization Catalyst with its Methylated Boralumoxane Counterion

Keywords: aluminum • homogeneous catalysis • metallocenes • polymerization • zirconium

---

Using the irreversible formation of an alkane, the proton-removing ability of a magnesiated amine, and the activating effect of a carboxamido group, weakly acidic CH groups in a variety of systems can be selectively converted into useful amido-Grignard reagents (see scheme; DAH = dehydrated diisopropylamine).



Angew. Chem. **2002**, *114*, 2273 – 2275

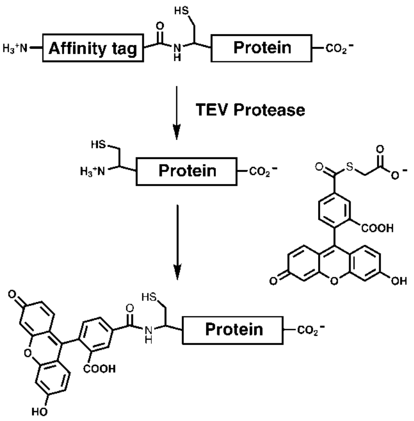
M.-X. Zhang, P. E. Eaton* 2169 – 2171

$BuMgNiPr_2$: A New Base for Stoichiometric, Position-Selective Deprotonation of Cyclopropane Carboxamides and Other Weak CH Acids

Keywords: amides • cyclopropanes • Grignard reagents • magnesiation • metalation

---

The highly selective tobacco etch virus NIa protease (TEV protease) can be used to remove affinity tags with mutated cleavage sites to produce proteins for site-specific labeling and chemoselective ligations (see scheme). This provides a simple, efficient method for producing proteins with N-terminal cysteines for proteomic applications.



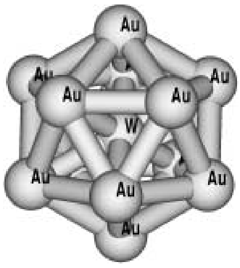
Angew. Chem. **2002**, *114*, 2275 – 2278

T. J. Tolbert, C.-H. Wong* 2171 – 2174

New Methods for Proteomic Research: Preparation of Proteins with N-Terminal Cysteines for Labeling and Conjugation

Keywords: amino acids • chemoselectivity • nanotechnology • proteins • proteomics

A new class of molecules, WAu_{12} (see picture) and its isoelectronic analogues, has been proposed and theoretically studied. The calculated radial W–Au distance is unusually short, 268 pm at the best level of theory. The frontier orbitals, both HOMO and LUMO, have fivefold degenerate h_g symmetry. The gap between them approaches 3 eV. Possible applications of these isoelectronic clusters are discussed.



Angew. Chem. **2002**, *114*, 2278–2280

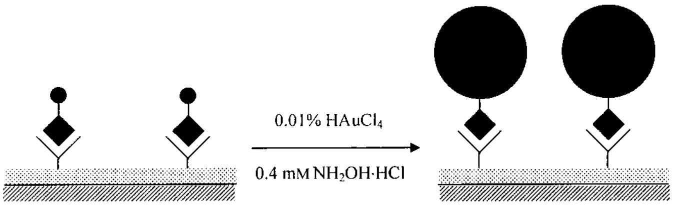
P. Pyykkö,* N. Runeberg 2174–2176

Icosahedral WAu_{12}: A Predicted Closed-Shell Species, Stabilized by Aurophilic Attraction and Relativity and in Accord with the 18-Electron Rule

Keywords: cluster compounds · gold · icosahedral symmetry · nanostructures · tungsten

---

Growing gold: Human immunoglubulin G (h-IgG) can be detected by the naked eye after enlarging Au nanoparticles in vitro with $HAuCl_4/NH_2OH \cdot HCl$, which immobilizes the Au nanoparticles on the nitrocellulose filter (see scheme; ● = Au nanoparticle, ◆ = anti-h-IgG, Y = h-IgG). The detection limit of approximately 10 pg mL^{-1} rivals the limits of fluorescent, radioactive, and enzyme-colorometric methods.



Angew. Chem. **2002**, *114*, 2280–2283

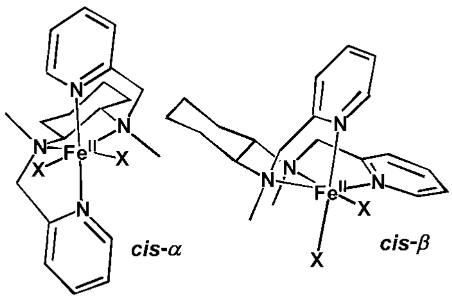
Z. Ma, S.-F. Sui* 2176–2179

Naked-Eye Sensitive Detection of Immunoglubulin G by Enlargement of Au Nanoparticles In Vitro

Keywords: gold · immunoglobulins · nanoparticles · particle enlargement · sensors

---

Quite unexpectedly, the topology of the tetradentate ligand in [Fe^{II}(bpmcn)$(OTf)_2$] (bpmcn = *N,N′*-bis-(2-pyridylmethyl)-*N,N′*-dimethyl-*trans*-1,2-diaminocyclohexane), whether *cis-α* or *cis-β* (see picture), determines the course of catalytic alkane hydroxylation and olefin oxidation reactions with H_2O_2, which afford products with varying stereoselectivity and dramatically different sources of incorporated oxygen. These results demonstrate the exquisite role ligands can play in the fine tuning of the reactivity of an iron catalyst.



Angew. Chem. **2002**, *114*, 2283–2285

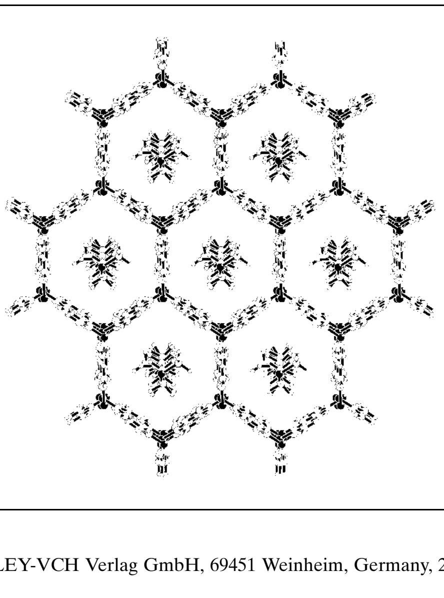
M. Costas, L. Que, Jr.* 2179–2181

Ligand Topology Tuning of Iron-Catalyzed Hydrocarbon Oxidations

Keywords: homogeneous catalysis · iron · ligand effects · oxidation · reaction mechanisms

---

Designed bilayer structure: The formation of a bilayer structure is reported, in which two guest molecules are contained within each local segment of tunnel within a layered urea host structure (one layer of which is shown in the picture). One novel feature of this structure is a locally empty region within the urea host tunnel, which arises from a significant van der Waals "gap" between adjacent guest molecules within the bilayer.



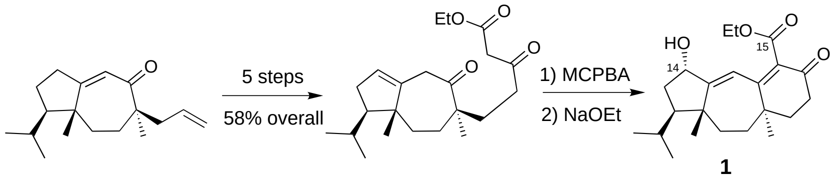
Angew. Chem. **2002**, *114*, 2285–2288

S.-O. Lee, B. M. Kariuki,
K. D. M. Harris* 2181–2184

Design of a Bilayer Structure in an Organic Inclusion Compound

Keywords: host–guest systems · hydrogen bonds · inclusion compounds · solid-state structures · urea

Some serious and unexpected complications emerged in the key annulation step required to reach **1**, the core of guanacastepene A (see scheme). The solution to these problems concurrently solved the major issues associated with the different oxidation states of C14 and C15. Although the authors have not generalized this type of annulation, it could have broad applications to building incrementally oxygenated polycyclic natural products.



Angew. Chem. **2002**, *114*, 2289–2292

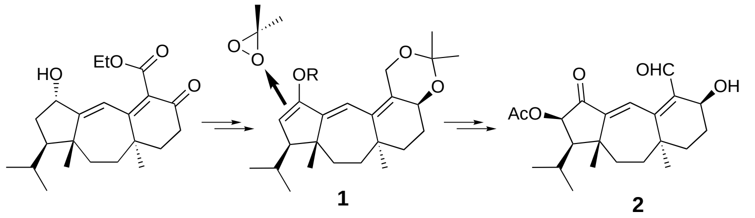
D. S. Tan, G. B. Dudley,
S. J. Danishefsky* 2185–2188

Synthesis of the Functionalized Tricyclic Skeleton of Guanacastepene A: A Tandem Epoxide-Opening β-Elimination/Knoevenagel Cyclization

Keywords: antibiotics · cyclization · natural products · oxidation · total synthesis

---

An external oxidant approaches *syn* to the isopropyl and methyl substituents on the five-membered ring of **1**. This surprising and selective epoxidation was exploited in the total synthesis of guanacastepene A (**2**).



Angew. Chem. **2002**, *114*, 2292–2295

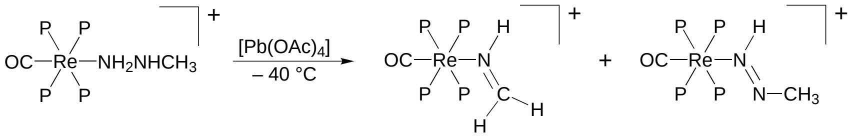
S. Lin, G. B. Dudley, D. S. Tan,
S. J. Danishefsky* 2188–2191

A Stereoselective Route to Guanacastepene A through a Surprising Epoxidation

Keywords: antibiotics · diastereoselectivity · epoxidation · natural products · total synthesis

---

Unexpectedly, oxidation of the coordinated methylhydrazine group in the $[Re(CH_3NHNH_2)(CO)P_4]BPh_4$ ($P = P(OEt)_3$) complex by $Pb(OAc)_4$ at −40°C affords not only the methyldiazene $[Re(CH_3N{=}NH)(CO)P_4]^+$ ion, but also the methyleneimine $[Re(\eta^1\text{-}NH{=}CH_2)(CO)P_4]^+$ derivative (see scheme), which was isolated and characterized by spectroscopy and X-ray crystallography.



Angew. Chem. **2002**, *114*, 2296–2298

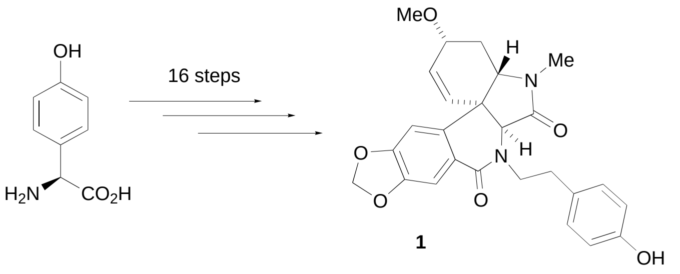
G. Albertin,* S. Antoniutti, A. Bacchi,
E. Bordignon, M. T. Giorgi,
G. Pelizzi 2192–2194

Methyleneimine $CH_2{=}NH$ as a Unidentate Ligand in Rhenium Complexes

Keywords: imines · N ligands · oxidation · P ligands · rhenium

---

A sequence of polymer-supported reagents and scavengers was used to promote the synthetic transformations in the first total synthesis of (+)-plicamine (**1**), a member of the amaryllidaceae alkaloid family, starting from L-4-hydroxyphenylglycine (see scheme).



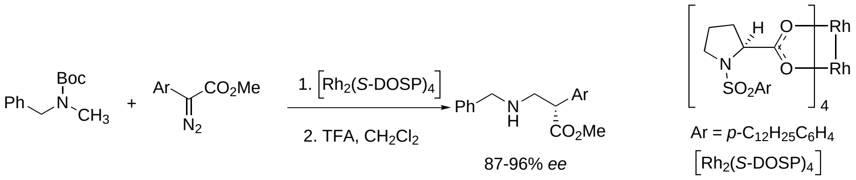
Angew. Chem. **2002**, *114*, 2298–2301

I. R. Baxendale, S. V. Ley,*
C. Piutti 2194–2197

Total Synthesis of the Amaryllidaceae Alkaloid (+)-Plicamine and Its Unnatural Enantiomer by Using Solid-Supported Reagents and Scavengers in a Multistep Sequence of Reactions

Keywords: alkaloids · scavengers · solid-supported reagents · synthetic methods · total synthesis

A very direct approach for the synthesis of β-amino esters is provided by catalytic asymmetric C–H activation by means of carbenoid-induced C–H insertion (see scheme; Boc = butyloxycarbonyl; TFA = trifluoroacetic acid). The reactions described herein represent the first regioselective intermolecular C–H insertions occurring at a methyl site.



Angew. Chem. **2002**, *114*, 2301 – 2303

H. M. L. Davies,*
C. Venkataramani .... 2197 – 2199

Catalytic Enantioselective Synthesis of β^2-Amino Acids

Keywords: amino acids · asymmetric catalysis · C–H activation · insertion · rhodium

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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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