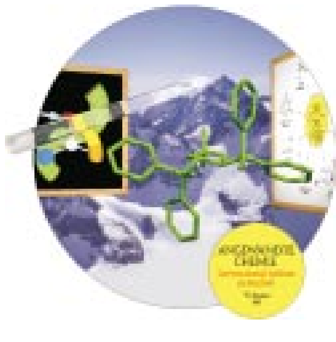
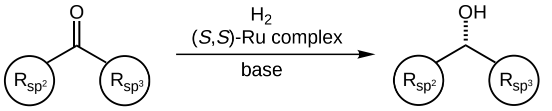
COVER PICTURE

The cover picture shows a model of the “progenitor-TADDOLs” in front of a panorama of the Fünffingersstocks and the Wenden Glacier in the Titlisgebiet (Switzerland). The model is flanked by a stylized view of the general mechanistic model for the preferred stereochemical pathway of the Ti–TADDOLate-catalyzed reaction of chelating substrates (left) and a blackboard (right) showing formulae of compounds that can be prepared with high enantioselectivity by nucleophilic addition in the presence of titanium TADDOLates. From TADDOL, introduced in 1982, a genuine auxiliary system for the “introduction of chirality” (not only by reaction) has been developed, which, in the final sprint against the competition has a good chance of securing a place on the winning podium. The photograph of the mountain landscape was taken by Dr. J. Frackenpohl, the cover picture was generated by one of the authors (A.H.) of the comprehensive review of TADDOLs in this issue (p. 92 ff.) with the help of the program Povray.



REVIEWS

No interaction with the metal center is necessary for the rapid, productive, and stereoselective catalytic hydrogenation of simple ketones when these reactions are carried out in the presence of complexes of general form [RuCl$_2$(phosphane)$_2$(1,2-diamine)]. The combined use of a BINAP ligand and a chiral 1,2-diamine allows for asymmetric hydrogenation of a wide range of aromatic, heteroaromatic, and olefinic ketones to the corresponding chiral alcohols with high enantiomeric excess [Eq. (1)]. R_{sp^2} = aryl, heteroaryl, alkenyl; R_{sp^3} = alkyl; Ar = 3,5-(CH$_3$)$_2$C$_6$H$_3$.



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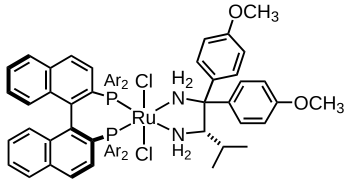


(*S*,*S*)-Ru complex

Angew. Chem. **2001**, *113*, 41–75

R. Noyori,* T. Ohkuma 40–73

Asymmetric Catalysis by Architectural and Functional Molecular Engineering: Practical Chemo- and Stereoselective Hydrogenation of Ketones

Keywords: asymmetric hydrogenation · carbonyl hydrogenation · P ligands · ruthenium · synthetic methods

---

Mimicking nature: The encapsulation of an active site within a protein shell is a well-known structural motif in enzymology. During the last decade considerable advances have been made in using the unique architecture of a dendrimer to shield photo-, electro-, or catalytically active core moieties (see schematic representation). This area of research has led to many new discoveries spanning the design of biological mimics to the construction of optoelectronic devices.

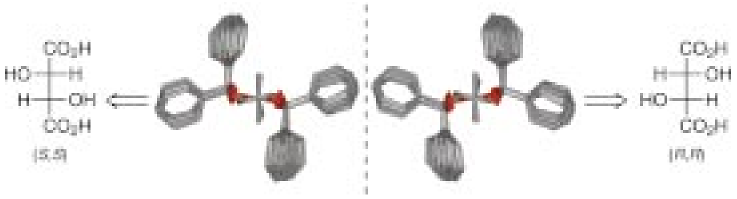
Angew. Chem. **2001**, *113*, 76–94

S. Hecht, J. M. J. Fréchet* 74–91

Dendritic Encapsulation of Function: Applying Nature’s Site Isolation Principle from Biomimetics to Materials Science

Keywords: dendrimers · materials science · molecular devices · structure–property relationships

Since their discovery nearly 20 years ago TADDOLs and their derivatives have revealed themselves to be true chiral auxiliary systems. Compounds of this type are accessible from tartaric acid with an almost unlimited degree of structural variety. They serve not only as homogeneous and solid phase bound chiral reagents and ligands for stoichiometric and catalytic applications, but also assist in creating cholesteric phases and host lattices capable of distinguishing between enantiomeric inclusions or facilitating enantioselective solid-phase reactions. The availability of over 120 crystal structures (see the overlays in the picture) makes it possible to discuss mechanistic models for courses of the various reactions.



Angew. Chem. **2001**, *113*, 96–142

D. Seebach,* A. K. Beck,
A. Heckel 92–138

TADDOLs, Their Derivatives, and TADDOL Analogues: Versatile Chiral Auxiliaries

Keywords: asymmetric catalysis · asymmetric synthesis · enantiomer separation · TADDOLs

ESSAY

The evaluation of the publications in *Angewandte Chemie* as well as the journal as a whole, in terms of the numbers of citations in the Science Citation Index (SCI) and the Journal Impact Factor (JIF), are studied with regard to errors resulting from the publication of two editions of the journal.

Angew. Chem. **2001**, *113*, 143–148

W. Marx* 139–143

Angewandte Chemie in Light of the Science Citation Index

Keywords: impact factor · literature searches · science citation index

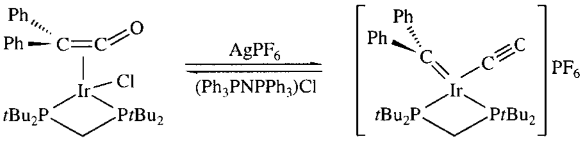
VIPs

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

Scandium Carbide Endohedral Metallofullerenes $(Sc_2C_2)@C_{84}$	C.-R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara*	◆
Towards the Development of Antitumor Vaccines: A Synthetic Conjugate of a Tumor-Associated MUC1 Glycopeptide Antigen with the Tetanus Toxin Epitope	S. Keil, C. Claus, W. Dippold, H. Kunz*	◆
Synthesis and Structure of a $Ga_{84}R_{20}^{4-}$ Cluster. A link between Metalloid Clusters and Fullerenes?	A. Schnepf and H. Schnöckel*	

HIGHLIGHTS

At a cationic ketene iridium(I) complex a fundamentally important reaction for organometallic chemistry, namely the metal-assisted reversible cleavage of a C–C double bond [Eq. (1)], has been illustrated for the first time. This study will probably initiate a reinvestigation of the elementary steps of the Fischer–Tropsch synthesis with the aim to find more appropriate catalysts for the selective generation of oxygen-containing products.



(1)

Angew. Chem. **2001**, *113*, 149–150

H. Werner,* E. Bleuel 145–147

Metal-Assisted Cleavage of a C–C Double Bond: Simple and Reversible

Keywords: carbene complexes · iridium · isomerization · ketene complexes · rhodium

---

A danger to cryptography is not yet present but theoretical concepts of quantum-information processing can be realized experimentally using the methods of NMR spectroscopy and these thereby usher in the quantum computer. The design and synthesis of compounds suitable to form the molecular basis of larger NMR quantum computers is an interesting, but far from trivial, challenge.

Angew. Chem. **2001**, *113*, 151–153

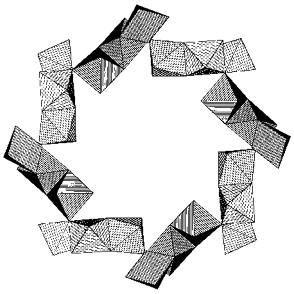
S. J. Glaser* 147–149

NMR Quantum Computing

Keywords: NMR spectroscopy · quantum computer · scalar coupling · through-bond interactions

COMMUNICATIONS

The highest nuclearity cyclic structure for the 3d metals is the Ni_{24} cage reported. It can be described as an octamer of trinuclear units (shown schematically), held together by metal–ligand bonds and a large number of hydrogen bonds.



Angew. Chem. **2001**, *113*, 155–158

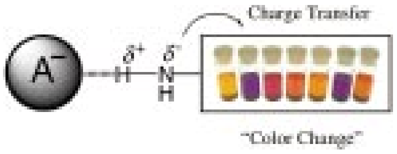
A. L. Dearden, S. Parsons,
R. E. P. Winpenny* 151–154

Synthesis, Structure, and Preliminary Magnetic Studies of a Ni_{24} Wheel

Keywords: hydrogen bonds · magnetic properties · nickel · N ligands · O ligands

---

No elaborate syntheses are required to generate colorimetric anion sensors. Rather, many commercially available chromophores (dyes) with built-in hydrogen bond donor sites have been found to act as “off-the-shelf” anion indicators (see scheme). These species allow for the so-called naked eye detection of fluoride, chloride, and phosphate anions under a range of conditions.



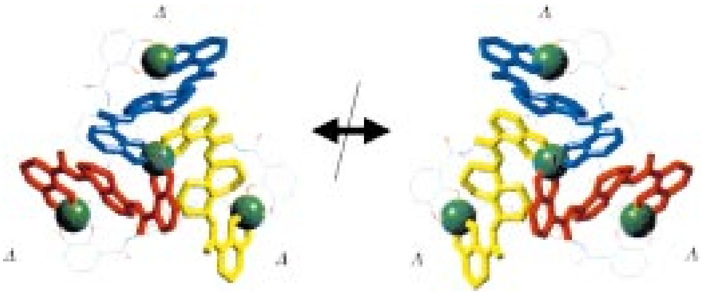
Angew. Chem. **2001**, *113*, 158–161

H. Miyaji, J. L. Sessler* 154–157

Off-the-Shelf Colorimetric Anion Sensors

Keywords: anions · charge transfer · hydrogen bonds · indicators · sensors

Enough mechanical stiffness that the metal centers can no longer racemize is provided by the connection of four labile metal centers (Al^{III}, Ga^{III}, In^{III}, Fe^{III}) and six achiral bis-catecholate ligands in a rigid tetrahedral assembly (see picture). The resolution and unprecedented kinetic stability of such a chiral supramolecular assembly is reported here for the first time.



Angew. Chem. **2001**, *113*, 161–164

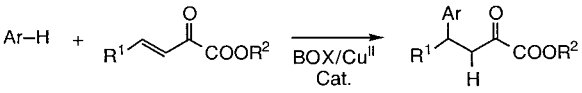
A. J. Terpin, M. Ziegler, D. W. Johnson,
K. N. Raymond* 157–160

Resolution and Kinetic Stability of a Chiral Supramolecular Assembly Made of Labile Components

Keywords: chiral resolution · cluster compounds · host–guest chemistry · kinetic stability · supramolecular chemistry

---

Useful catalytic BOXes: Chiral bisoxazoline (BOX)/Lewis acid complexes can catalyze highly enantioselective Friedel–Crafts alkylation reactions. The new reaction (see scheme) is successful with both aromatic and heteroaromatic compounds and with a wide range of β,γ-unsaturated α-ketoesters (R^1 = alkyl, aryl, or a protected alcohol). Products are formed with up to >99% *ee*.



Angew. Chem. **2001**, *113*, 164–167

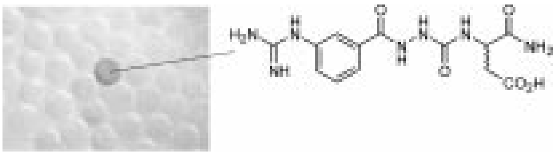
K. B. Jensen, J. Thorhauge, R. G. Hazell,
K. A. Jørgensen* 160–163

Catalytic Asymmetric Friedel–Crafts Alkylation of β,γ-Unsaturated α-Ketoesters: Enantioselective Addition of Aromatic C–H Bonds to Alkenes

Keywords: aromatic substitution · asymmetric catalysis · Friedel–Crafts alkylations · Lewis acids · synthetic methods

---

Libraries of low molecular weight aza-RGD mimetics were synthesized according to the split method and evaluated by on-bead screening with a soluble integrine receptor. No coding was required because the biologically active mimetics could be identified using MS^n after photochemical cleavage from the stained beads (see picture). New $\alpha_v\beta_3$ antagonists were found by this approach.



Angew. Chem. **2001**, *113*, 169–173

C. Gibson, G. A. G. Sulyok, D. Hahn,
S. L. Goodman, G. Hölzemann,
H. Kessler* 165–169

Nonpeptidic $\alpha_v\beta_3$ Integrin Antagonist Libraries: On-Bead Screening and Mass Spectrometric Identification without Tagging

Keywords: combinatorial chemistry · drug research · Integrins · mass spectrometry · peptide mimetics

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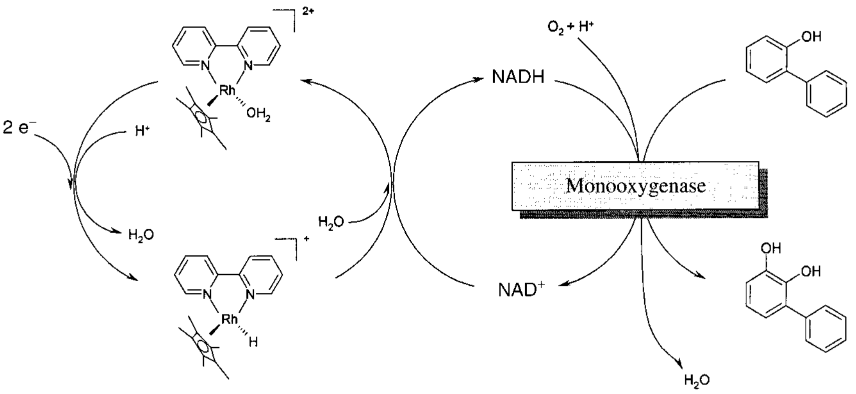
In oxygen-containing media the electrochemical regeneration of NADH is easier than expected, such that the regeneration procedure can even be applied to NAD(P)H-dependent monooxygenases (see scheme).



Angew. Chem. **2001**, *113*, 190–193

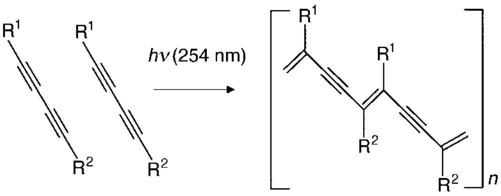
F. Hollmann, A. Schmid,*
E. Steckhan† 169–171

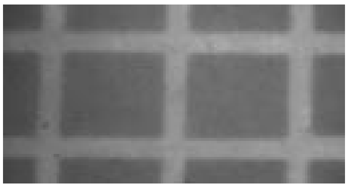
The First Synthetic Application of a Monooxygenase Employing Indirect Electrochemical NADH Regeneration

Keywords: coenzymes · electrochemistry · enzyme catalysis · hydroxylation · oxygenations

1433-7851/01/4001-0011 $ 17.50+.50/0

Micropatterned lipid bilayers have been created on solid supports by using lithographic polymerization of a diacetylene lipid (see picture). The domains of polymerized (light) serve, after removal of the monomers, as a two-dimensional master structure for the incorporation of biologically relevant lipid bilayer membranes.





Angew. Chem. **2001**, *113*, 184–186

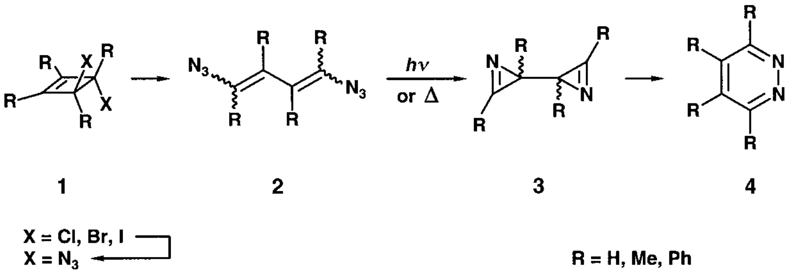
K. Morigaki,* T. Baumgart,
A. Offenhäusser, W. Knoll 172–174

Patterning Solid-Supported Lipid Bilayer Membranes by Lithographic Polymerization of a Diacetylene Lipid

Keywords: imprinting · lipids · membranes · microstructuring · polymerization

---

Highly strained and highly explosive: The highly strained heterocycles **3** are generated by thermolysis or photolysis of the azides **2** which resulted from ring cleavage of cyclobutenes **1**. Even at $-25°C$, the aromatization **3**→**4** occurs. On photochemical or silver-salt induced reactions, **3** can also be transformed into pyrimidines.



Angew. Chem. **2001**, *113*, 173–176

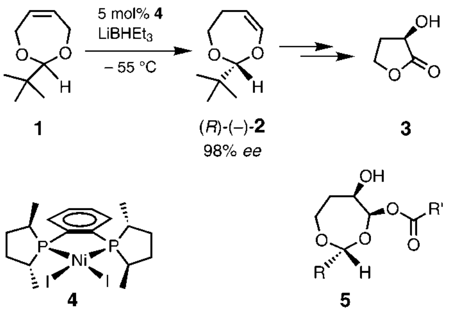
K. Banert,* F. Köhler 174–177

Synthesis of 1,4-Diazidobuta-1,3-dienes by Electrocyclic Ring Opening: Precursors for Bi-2*H*-azirin-2-yls and Their Valence Isomerization to Diazabenzenes

Keywords: azides · electrocyclic reactions · nitrogen heterocycles · photochemistry · valence isomerization

---

A breakthrough in the asymmetric isomerization of 4,7-dihydro-1,3-dioxepins **1** was achieved by using DuPHOS-modified dihalogenonickel complexes such as **4** as catalyst precursors. The absolute configurations of the isomerization products were determined by transforming **2** into 2-hydroxy-γ-butyrolactone **3** and 1,2,4-butanetriol through a new oxidation-ring contraction sequence. The relative configuration of the oxidation product **5** was established by crystal structure analysis.



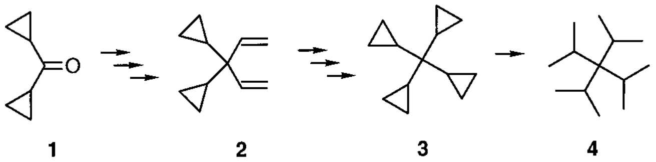
Angew. Chem. **2001**, *113*, 176–178

H. Frauenrath,* D. Brethauer, S. Reim,
M. Maurer, G. Raabe 177–179

Highly Enantioselective Isomerization of 4,7-Dihydro-1,3-dioxepins Catalyzed by Me-DuPHOS-Modified Dihalogenonickel Complexes and Determination of the Absolute Configuration of the Isomerization Products

Keywords: asymmetric catalysis · heterocycles · isomerization · nickel · ring contraction

Surprising symmetry, surprising synthesis: Dicyclopropyldiethenylmethane (**2**), prepared from dicyclopropylketone (**1**) in several steps, was successfully cyclopropanated with a large excess of diazomethane in the presence of palladium(II) acetate yielding the structurally interesting tetracyclopropylmethane (**3**; 92 % yield). Upon catalytic hydrogenation, **3** was quantitatively converted into tetraisopropylmethane (**4**). X-ray structure analysis established S_4 symmetry for **3** and D_{2d} symmetry for **4**, in excellent agreement with the B3LYP/6-31+G** computed structures.



Angew. Chem. **2001**, *113*, 179–182

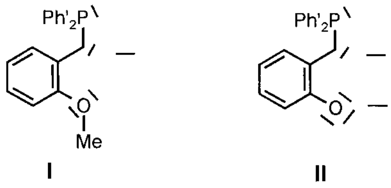
S. I. Kozhushkov, R. R. Kostikov,
A. P. Molchanov, R. Boese,
J. Benet-Buchholz, P. R. Schreiner,
C. Rinderspacher, I. Ghiviriga,
A. de Meijere* 180–183

Tetracyclopropylmethane: A Unique Hydrocarbon with S_4 Symmetry

Keywords: ab initio calculations · alkenes · cyclopropanation · hydrogenations · small ring systems

---

Hard and soft centers: the donors O (hard), P and C (soft) are together in the multidentate, oxygen-substituted, anionic phosphanes **I** and **II**, which are particularly suitable for the synthesis of novel calcium organyls. With these mono- and dianionic ligands calcium organyl compounds, without cyclopentadiene ligands, could be prepared and structurally characterized: a sodium trialkyl calcate(II) and the first calcium organyl compound with a heterocubane structure. Ph' = *p*-tolyl.



Angew. Chem. **2001**, *113*, 187–190

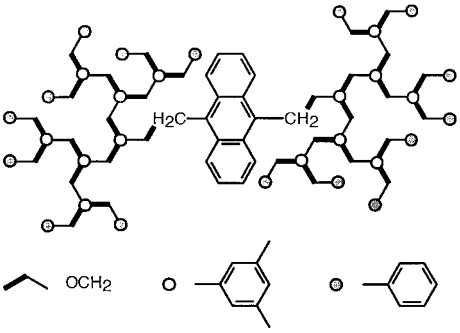
V. Knapp, G. Müller* 183–186

Cyclopentadienyl-Free Calcium Alkyls with Heteroelement-Substituted Anionic Phosphane Ligands: Synthesis and Structure of a Trialkyl Calcate(II) and of an Organocalcium Heterocubane

Keywords: alkaline earth metals · ate complexes · calcium · cubane

---

A remarkable antenna effect observed in dendrimers with an anthracene core and dendrons of the Fréchet type (see picture) results in strongly increased fluorescence quantum yields relative to that of anthracene. The UV-induced [4π+4π] cycloaddition, in which the anthracene core reacts with a benzene ring of the dendrons, leads to novel photodimers.



Angew. Chem. **2001**, *113*, 193–195

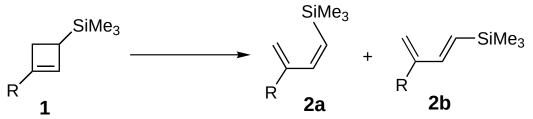
D. Cao, H. Meier* 186–188

The Unusual Photochemistry of Dendrimers with an Anthracene Core

Keywords: cycloadditions · dendrimers · energy transfer · photodimerization

---

A preference for inward over outward rotation is found for the thermal conrotatory ring-opening reaction of 1-cyclobutene **1**, to produce 1,3-butadiene **2**, when a silyl substituent is located at the 3-position. This preference exists in spite of the bulkiness of the substituent.



Angew. Chem. **2001**, *113*, 182–184

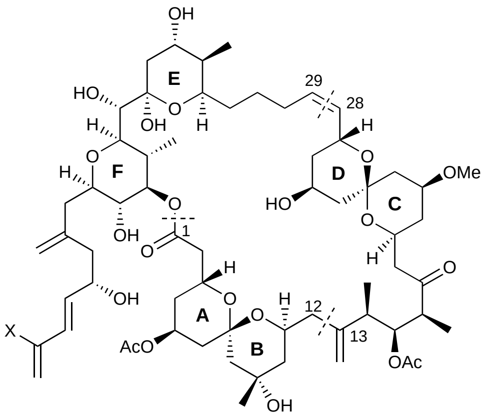
M. Murakami,* Y. Miyamoto,
Y. Ito* 189–190

A Silyl Substituent Can Dictate a Concerted Electrocyclic Pathway: Inward Torquoselectivity in the Ring Opening of 3-Silyl-1-cyclobutene

Keywords: density functional calculations · electrocyclic reactions · hyperconjugation · silicon · substituent effects

1433-7851/01/4001-0013 $ 17.50+.50/0

An advanced ABCD fragment (see picture) constructed on the way to the total synthesis of the potent antitumor agent (+)-spongistatin 2 has also been used in a formal total synthesis of (+)-spongistatin 1. In both cases the critical step was an acid-mediated epimerization in the presence of Ca^{2+} ions to stabilize the axial–equitorial CD spiroketal.



Spongistatin 1, X = Cl
Spongistatin 2, X = H

A. B. Smith III,* V. A. Doughty, Q. Lin, L. Zhuang, M. D. McBriar, A. M. Boldi, W. H. Moser, N. Murase, K. Nakayama, M. Sobukawa 191–195

The Spongistatins: Architecturally Complex Natural Products—Part One: A Formal Synthesis of (+)-Spongistatin 1 by Construction of an Advanced ABCD Fragment

A. B. Smith III,* Q. Lin, V. A. Doughty, L. Zhuang, M. D. McBriar, J. K. Kerns, C. S. Brook, N. Murase, K. Nakayama 196–199

The Spongistatins: Architecturally Complex Natural Products—Part Two: Synthesis of the C(29–51) Subunit, Fragment Assembly, and Final Elaboration to (+)-Spongistatin 2

Angew. Chem. **2001**, *113*, 197–201

Angew. Chem. **2001**, *113*, 202–205

Keywords: antitumor agents · macrocycles · natural products · total synthesis

---

A closed spherical structure which can self-maintain or grow/reproduce depending upon the chemical parameter setting would be a simple chemical model of the homeostatic cell. One such model is presented here. It is based on oleic acid/oleate vesicles which host two competitive reactions which take place within the boundary of the bilayer, that is, one reaction which produces more vesicles and one which destroys them.

Angew. Chem. **2001**, *113*, 205–208

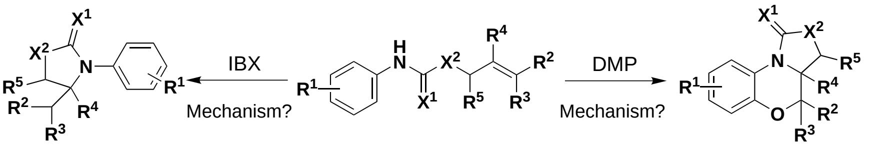
H. H. Zepik, E. Blöchliger, P. L. Luisi * 199–202

A Chemical Model of Homeostasis

Keywords: biomimetic synthesis · homeostasis · liposomes · nanostructures · supramolecular chemistry

---

The intriguing mechanisms by which *o*-iodoxybenzoic acid (IBX) and Dess–Martin periodinane (DMP) transform anilides to heterocyclic systems (see scheme) have been extensively studied and elucidated, which has led to the design of further synthetic technologies.



Angew. Chem. **2001**, *113*, 208–212

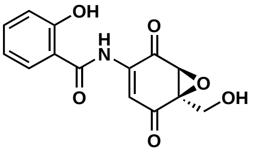
K. C. Nicolaou,* P. S. Baran, R. Kranich, Y.-L. Zhong, K. Sugita, N. Zou 202–206

Mechanistic Studies of Periodinane-Mediated Reactions of Anilides and Related Systems

Keywords: anilides · heterocycles · iodine reagents · oxidations · reaction mechanisms

---

A mechanistically inspired tandom Dess–Martin periodinane (DMP) induced oxidation sequence converts anilides into *N*-substituted *p*-quinones or *o*-azaquinones depending on the aromatic nucleus substitution. The application of this technology resulted in an expedient total synthesis of the potent anti-arthritic agent epoxyquinomycin B (see picture).



epoxyquinomycin B

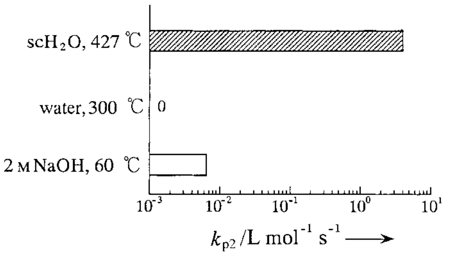
Angew. Chem. **2001**, *113*, 213–216

K. C. Nicolaou,* K. Sugita, P. S. Baran, Y.-L. Zhong 207–210

New Synthetic Technology for the Construction of N-Containing Quinones and Derivatives Thereof: Total Synthesis of Epoxyquinomycin B

Keywords: iodine reagents · natural products · oxidations · quinones · total synthesis

Catalyst and reaction medium in one: that is the dual role of supercritical water (scH_2O) in the disproportionation of benzaldehyde. In the near-critical region the reaction rates (k_{p2}) are significantly greater than those found in water and aqueous NaOH (see picture, values for scH_2O and water are at 25 MPa), also unequivocal chemical evidence for the participation of the OH^- ion, not the $OH^\bullet$ radical, is obtained.



Angew. Chem. **2001**, *113*, 216–219

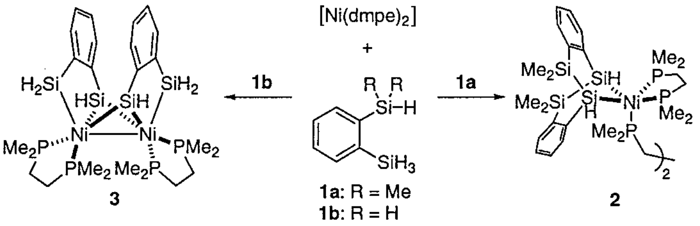
Y. Ikushima,* K. Hatakeda, O. Sato, T. Yokoyama, M. Arai 210–213

Structure and Base Catalysis of Supercritical Water in the Noncatalytic Benzaldehyde Disproportionation Using Water at High Temperatures and Pressures

Keywords: aldehydes · disproportionation reactions · IR spectroscopy · reaction mechanisms · supercritical fluids

---

An eight-membered cyclic dimer of the hydrosilane **1a** is produced through dehydrogenative Si–Si bond formation during the reaction of **1a** with a nickel complex to give **2**. A possible intermediate in this dehydrocoupling reaction is the dinuclear silyl(μ-silylene)nickel(III) complex **3**, which could be isolated from the reaction of the analogous hydrosilane **1b** with [Ni(dmpe)$_2$]. dmpe = 1,2-bis(dimethylphosphanyl)ethane.



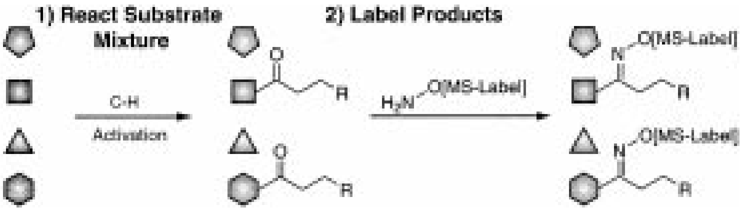
Angew. Chem. **2001**, *113*, 219–222

S. Shimada, M. L. N. Rao, T. Hayashi, M. Tanaka* 213–216

Isolation of Dinuclear (μ-Silylene)(silyl)nickel Complexes and Si–Si Bond Formation on a Dinuclear Nickel Framework

Keywords: dimerizations · nickel · silicon

The functional groups and heterocyclic classes known to be compatible with a directed C–H activation with [Ru$_3$(CO)$_{12}$] has been expanded through development of a new substrate screening strategy. Following C–H activation, a library of products is MS-labeled and rapidly evaluated by positive ion electrospray ionization mass spectrometry (see scheme) to directly identify successful products and their yields.



Angew. Chem. **2001**, *113*, 222–225

J. W. Szewczyk, R. L. Zuckerman, R. G. Bergman,* J. A. Ellman* 216–219

A Mass Spectrometric Labeling Strategy for High-Throughput Reaction Evaluation and Optimization: Exploring C–H Activation

Keywords: C–H activation · combinatorial chemistry · high-throughput screening · mass spectrometry

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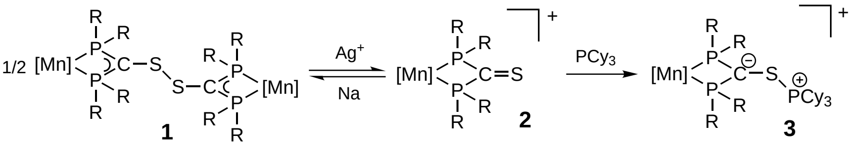
An isolated reaction intermediate in the desulfurization of thiones promoted by phosphanes is provided by the ylide derivative **3**, which is obtained by thiophilic addition of PCy$_3$ to **2**. Complex **2** is formed from the disulfide-containing dimetallic complex **1** by scission of the S–S bond. [Mn] = Mn(CO)$_4^+$, R = Ph.



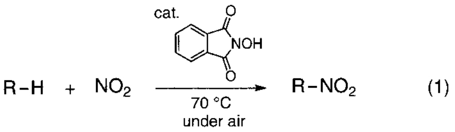
Angew. Chem. **2001**, *113*, 226–228

J. Ruiz,* M. Ceroni, O. V. Quinzani, V. Riera, O. E. Piro 220–222

Reversible S–S Bond Breaking and Bond Formation in Disulfide-Containing Dinuclear Complexes of Mn^I

Keywords: manganese · phosphanes · sulfur · ylides

Higher alkanes such as cyclohexane, cyclooctane, and adamantane undergo nitration with NO_2 in the presence of a catalytic amount of *N*-hydroxyphthalimide to form the corresponding nitroalkanes [Eq. (1)]. Furthermore, the nitration is conducted under air, and NO generated in the course of the reaction can be reoxidized by O_2 to NO_2, and thus reused in the nitration.



Angew. Chem. **2001**, *113*, 228–230

S. Sakaguchi, Y. Nishiwaki, T. Kitamura, Y. Ishii* 222–224

Efficient Catalytic Alkane Nitration with NO_2 under Air Assisted by *N*-Hydroxyphthalimide

Keywords: catalysts · hydrocarbons · nitrations · nitrogen oxides · radicals

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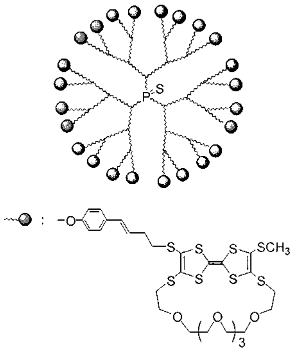
Electrodeposition of dendrimers containing redox-active tetrathiafulvalene units and coordinating crown ether moieties provides a novel strategy for producing modified electrodes that respond to the presence of a particular metal cation. Application of the third-generation dendrimer (see schematic diagram) to platinum gave an electrode whose first oxidation potential is a function of Ba^{2+} concentration in the range $(1-8) \times 10^{-4}$ M.



Angew. Chem. **2001**, *113*, 230–233

F. Le Derf, E. Levillain, G. Trippé, A. Gorgues, M. Sallé,* R.-M. Sebastían, A.-M. Caminade, J.-P. Majoral* 224–227

Immobilization of Redox-Active Ligands on an Electrode: The Dendrimer Route

Keywords: dendrimers · electrochemistry · immobilizations · O ligands · sensors

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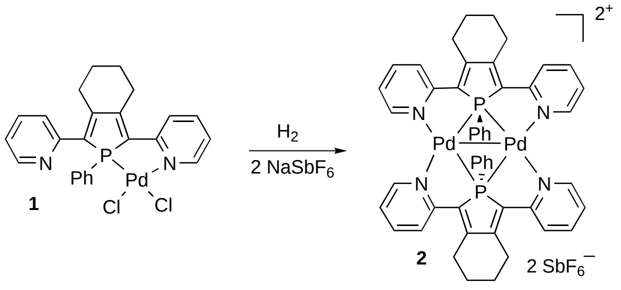
A simple reduction of the Pd^{II} complex **1** affords the Pd^{I} dimer **2**, featuring a μ_2 symmetrically bridging phosphole unit, and thus a novel coordination mode for a tertiary phosphane. Complex **2** appears to be very stable towards additional ligands such as CO and PPh_3, and the structural data are in accordance with calculations, which reveal that the Pd–Pd and Pd–P bonding is highly delocalized.



Angew. Chem. **2001**, *113*, 234–237

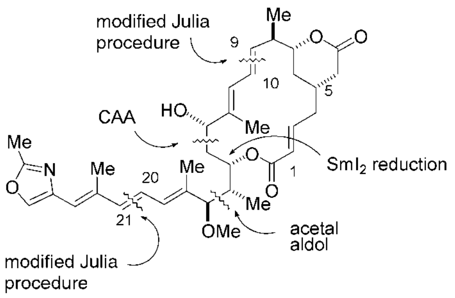
M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J.-F. Halet,* R. Réau* 228–231

A Rare Phosphane Coordination Mode: A Symmetrically μ_2-Bridging Phosphole in a Dinuclear Palladium(I) Complex

Keywords: coordination modes · density functional calculations · palladium · phosphorus heterocycles · tridentate ligands

---

Catalytic asymmetric allylation (CAA) using tributyl-(2-ethylallyl)-stannane as a methyl ethyl ketone equivalent plays a key role in this synthesis of rhizoxin D. A subsequent substrate-directed acetal aldol reaction, fragment assembly by a modified Julia procedure, and directed electron transfer reduction are used to complete the synthesis (see scheme).



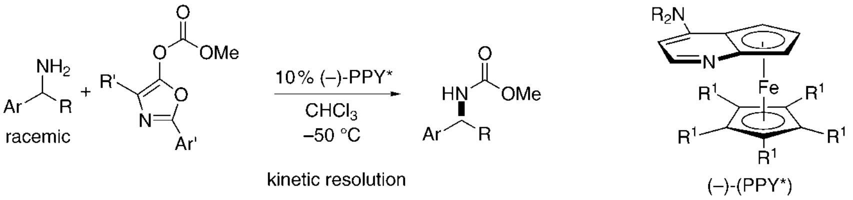
Angew. Chem. **2001**, *113*, 237–240

G. E. Keck,* C. A. Wager, T. T. Wager, K. A. Savin, J. A. Covel, M. D. McLaws, D. Krishnamurthy, V. J. Cee . . . 231–234

Asymmetric Total Synthesis of Rhizoxin D

Keywords: allylation · antitumor agents · asymmetric catalysis · samarium · total synthesis

A planar-chiral DMAP derivative, in conjunction with a readily available, novel acylating agent, effects the kinetic resolution of α-arylamines, a biologically important class of compounds, with a selectivity factor of up to 27 (see scheme). The catalyst used, PPY*, is the first effective nonenzymatic catalyst for the enantioselective acylation of amines. DMAP = 4-dimethylaminopyridine.



Angew. Chem. **2001**, *113*, 240–242

S. Arai, S. Bellemin-Laponnaz,
G. C. Fu* 234–236

Kinetic Resolution of Amines by a Nonenzymatic Acylation Catalyst

Keywords: acylations · amines · catalysts · chirality · kinetic resolution

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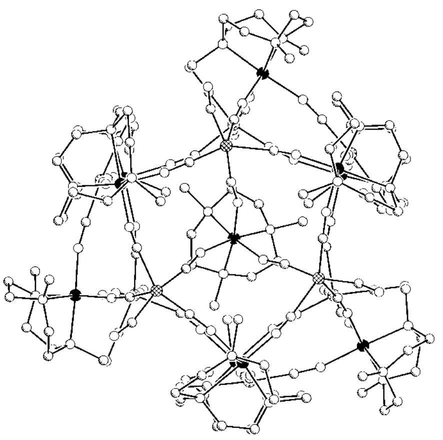
Unprecedented geometries are displayed by two chromium–nickel–cyanide clusters that have recently been synthesized. $[(Me_3tacn)_8Cr_8Ni_5(CN)_{24}]^{10+}$ exhibits a face-centered cubic structure with a Ni^{2+} ion missing from one face. This species reacts with $[Ni(CN)_4]^{2-}$ to yield $[(Me_3tacn)_{10}Cr_{10}Ni_9(CN)_{42}]^{6+}$ (shown in the picture), incorporating square-pyramidal and trigonal-bipyramidal $[Ni(CN)_5]^{3-}$ and square-planar $[Ni(CN)_4]^{2-}$ units in the largest metal–cyanide cluster reported to date. Me$_3$tacn = *N*,*N'*,*N''*-trimethyl-1,4,7-triazacyclononane.



Angew. Chem. **2001**, *113*, 242–245

J. J. Sokol, M. P. Shores,
J. R. Long* 236–239

High-Nuclearity Chromium–Nickel–Cyanide Clusters: An Open $Cr_8Ni_5(CN)_{24}$ Cage and a C_3-Symmetric $Cr_{10}Ni_9(CN)_{42}$ Cluster Incorporating Three Forms of Cyanonickelate

Keywords: cage compounds · cluster compounds · coordination chemistry · cyanides · magnetic properties

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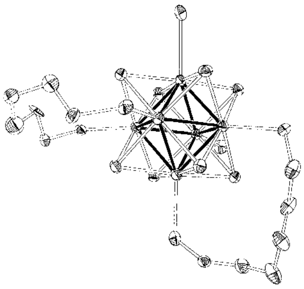
Substitution of the iodide ions in the octahedral hexarhenium cluster $[Re_6Se_8I_6]^{3-}$ by the diphosphane $Ph_2P(CH_2)_nPPh_2$ generates "bridge–chelate" complexes when $n = 6$ (dpph) with general formula $[Re_6Se_8I_{6-2m}(\mu\text{-dpph})_m]^{2m-4}$ ($m = 1-3$; the picture shows the *trans* isomer for $m = 2$), whereas for $n = 5$ only a monodentate binding mode of the diphosphane is found. Stepwise substitution by dpph strongly affects the redox processes, while the photophysical properties associated with the $[Re_6Se_8]^{2+}$ core change only moderately.



Angew. Chem. **2001**, *113*, 245–248

Z.-N. Chen, T. Yoshimura, M. Abe,
Y. Sasaki,* S. Ishizaka, H.-B. Kim,
N. Kitamura 239–242

Chelate Formation around a Hexarhenium Cluster Core by the Diphosphane Ligand $Ph_2P(CH_2)_6PPh_2$

Keywords: cluster compounds · coordination modes · luminescence · P ligands · rhenium

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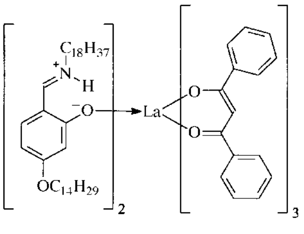
A monotropic smectic A phase is exhibited by adducts of tris(β-diketonato)lanthanide(III) complexes with a non-mesomorphic salicylaldimine Schiff base as Lewis base. Only four terminal alkyl chains were necessary in the Schiff base to induce mesomorphism in [La(dbm)$_3$] (see formula). Hdbm = 1,3-diphenyl-1,3-propanedione (dibenzoylmethane).



Angew. Chem. **2001**, *113*, 248–250

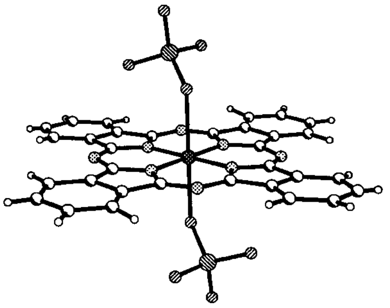
K. Binnemans,*
K. Lodewyckx 242–244

Coordinatively Unsaturated Metal Centers as Building Blocks for High Coordination Number Metallomesogens

Keywords: lanthanides · liquid crystals · metallomesogens · rare-earth compounds · supramolecular chemistry

One ring, two oxidations: The first doubly ring-oxidized metal phthalocyanine complex has been synthesized by galvanostatic electrocrystallization. Copper phthalocyanine was oxidized in the presence of perrhenate anions to form the new molecular compounds [Cu(pc)-(ReO$_4$)] and [Cu(pc)(ReO$_4$)$_2$] (structure shown). Single-crystal EPR results show that the oxidation of [Cu(pc)(ReO$_4$)$_2$] is entirely ring-based.

Angew. Chem. **2001**, *113*, 250–252



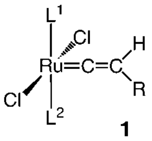
A. S. Gardberg, P. E. Doan,
B. M. Hoffman,* J. A. Ibers* .. 244–246

Singly and Doubly Oxidized Phthalocyanine (pc) Rings: [Cu(pc)(ReO$_4$)] and [Cu(pc)(ReO$_4$)$_2$]

Keywords: copper · electrocrystallization · EPR spectroscopy · oxidations · phthalocyanines

---

Ruthenium vinylidenes: metathesis catalysis on the bench? Ruthenium vinylidene compounds **1**, generated in situ from readily available, air-stable precursors, are used to catalyze ring-closing metathesis, ene–yne metathesis, cross-metathesis, and ring-opening metathesis polymerization. Bulky imidazolylidene ligands and terminal alkynes were found to be necessary components for achieving high catalytic activity.



1

Angew. Chem. **2001**, *113*, 253–255

J. Louie, R. H. Grubbs* 247–249

Highly Active Metathesis Catalysts Generated In Situ from Inexpensive and Air-Stable Precursors

Keywords: carbenes · homogeneous catalysis · metathesis · ruthenium · vinylidene complexes

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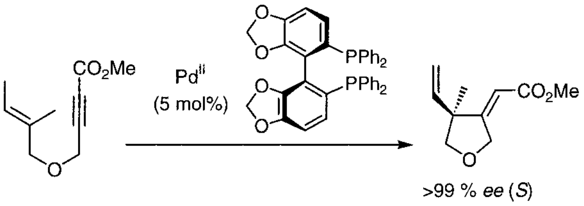
Enantioenriched five-membered rings with a quaternary chiral center are prepared with remarkable efficiency by the ene-type carbocyclization of 1,6-enynes catalyzed by chiral palladium complexes (see scheme). Possible mechanisms including neutral (five-coordinate) and cationic (four-coordinate) intermediates have also been proposed.



Angew. Chem. **2001**, *113*, 255–259

M. Hatano, M. Terada,
K. Mikami* 249–253

Highly Enantioselective Palladium-Catalyzed Ene-Type Cyclization of a 1,6-Enyne

Keywords: asymmetric catalysis · cyclizations · enynes · palladium

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

* Author to whom correspondence should be addressed

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