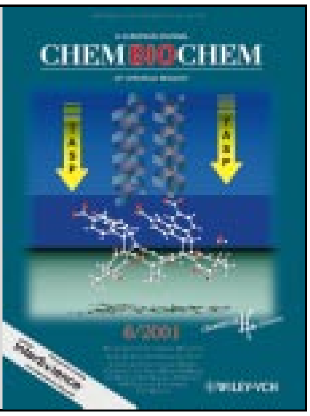
ANGEWANDTE
CHEMIE
INTERNATIONAL EDITION

A Journal of the
Gesellschaft
Deutscher Chemiker

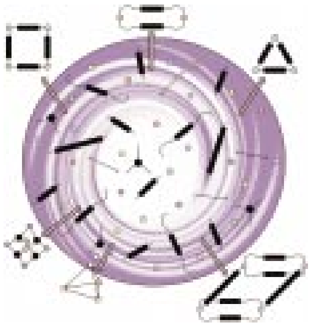
2001
40/11
Pages 1983–2184

ChemBioChem 6/2001 is bound
in this issue of *Angewandte Chemie.*

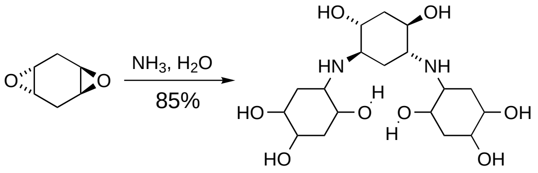


COVER PICTURE

The cover picture shows a swirling mixture of transition metal fragments and simple organic ligands that assemble into supramolecular coordination compounds, depicted on the perphery of the vortex. The synthesis of such large structures requires strategies that take into account the entropic costs of not forming higher ordered oligomers and polymers. The use of transition metal ions as building blocks for supramolecular compounds has become a widely practiced strategy for making such structures. Within this quickly growing field there have emerged three general synthetic approaches for the metal-directed formation of supramolecular coordination compounds. These are described by B. J. Holliday and C. A. Mirkin on p. 2022 ff.



Just a handful of good reactions are needed to assemble vast numbers of highly diverse organic molecules. (The graphic shows a simple example.) Yet, this easily accessible structural universe has not been mined by the medicinal chemistry community for its nuggets of desirable function. The requirements for the best reactions that can be employed, examples of such processes, and the philosophy that underlies their use are discussed in this review.



Angew. Chem. **2001**, *113*, 2056–2075

H. C. Kolb, M. G. Finn,
K. B. Sharpless* 2004–2021

Click Chemistry: Diverse Chemical Function from a Few Good Reactions

Keywords: combinatorial chemistry · drug research · synthesis design · water chemistry

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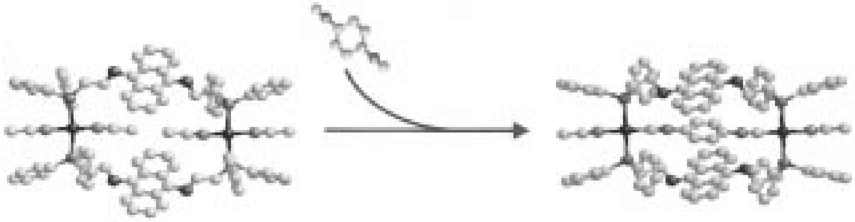
Supramolecular coordination complexes or coordination chemistry supramolecules? Emerging synthetic approches for the construction of supramolecular structures by coordination chemistry (see picture) have led to a rapid expansion of the field of suprarmolecular chemistry. Many structures are now accessible through the general principles that define these approaches, and the applications of the structures formed from them are beginning to be explored.



Angew. Chem. **2001**, *113*, 2076–2097

B. J. Holliday, C. A. Mirkin* 2022–2043

Strategies for the Construction of Supramolecular Compounds through Coordination Chemistry

Keywords: coordination chemistry · nanostructures · supramolecular chemistry · synthetic methods · transition metals

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VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Correlating Electron Transport and Molecular Structure in Organic Thin Films

R. E. Holmlin, R. F. Ismagilov, ◆
R. Haag, V. Mujica,
M. A. Ratner, M. A. Rampi*,
G. M. Whitesides*

Targeting Molecular Recognition: Exploring the Dual Role of Functional Pseudo-Prolines in the Design of SH3 Ligands

G. Tuchscherer,* D. Grell,
Y. Tatsu, P. Durieux,
J. Fernandez-Carneado,
B. Hengst, C. Kardinal, S. Feller*

HIGHLIGHTS

The ultimate goal of producing esters in 100 % yield from an equimolar reaction of carboxylic acid and alcohol may not be far away: The research groups of Yamamoto and Tanabe have found that effective condensation can be achieved using $HfCl_4 \cdot 2THF$ and diphenylammonium triflate catalysts, respectively. Although the first catalyst gives near quantitative yields of the esters (91 – > 99 %), the reaction is moisture sensitive, while the latter catalyst gives lower yields (89 – 96 %) but requires no dehydration reagents or equipment.

Angew. Chem. **2001**, *113*, 2099 – 2100

J. Otera * .... 2044 – 2045

In Search of Practical Esterification

Keywords: alcohols · carboxylic acids · esterification · homogeneous catalysis · synthetic methods

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Diverse complex systems may be studied by the new methods in solid-state NMR spectroscopy described herein. These methods use magic-angle spinning (MAS) on samples in oriented bilayers (right picture) and in orientationally disordered samples (left picture). Systems as diverse as uniformly $^{13}C,^{15}N$-labeled proteins, model membrane systems, and silk, as produced by the silkworm, can be structurally characterized.

Angew. Chem. **2001**, *113*, 2100 – 2105

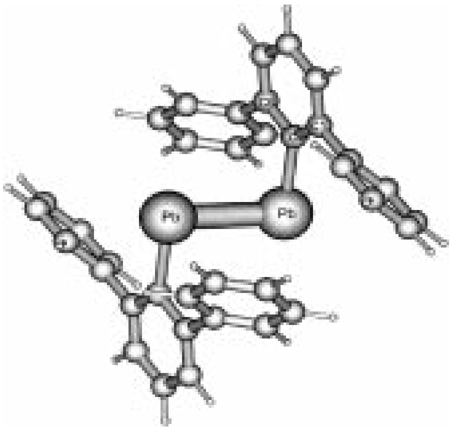
H. Schwalbe,* A. Bielecki .. 2045 – 2050

Recent Advances in High-Resolution Solid-State NMR Spectroscopy

Keywords: NMR spectroscopy · protein structures · structure elucidation

COMMUNICATIONS

Quantum-chemical calculations at the B3LYP level show that the bulky ligands $Ar^* = 2,6\text{-}Ph_2C_6H_3$ in Ar*PbPbAr* yield the *trans*-bent equilibrium structure shown as the lowest lying energy minimum form. There is no Pb–Pb π bond in Ar*PbPbAr*. The parent compounds PhPbPbPh and HPbPbH have doubly bridged energy minima structures.



Angew. Chem. **2001**, *113*, 2108 – 2112

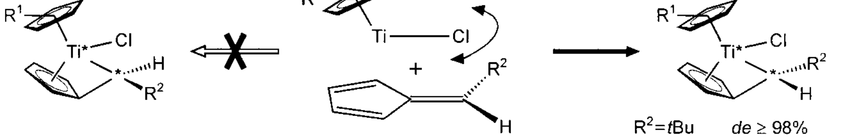
Y. Chen, M. Hartmann, M. Diedenhofen, G. Frenking * .... 2052 – 2055

Turning a Transition State into a Minimum—The Nature of the Bonding in Diplumbylene Compounds RPbPbR (R = H, Ar)

Keywords: bond theory · density functional calculations · diplumbylene · lead · multiple bonds

---

An alternative to the known thermally induced syntheses of fulvene complexes of early transition metals is now provided by the direct reductive complexation of pentafulvenes to [CpTiCl] fragments. These generally highly diastereoselective reactions (see scheme) enable a broad variation of substitution patterns and establish an extensive subsequent chemistry.



Angew. Chem. **2001**, *113*, 2112 – 2115

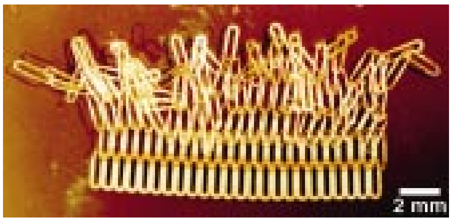
R. Beckhaus,* A. Lützen, D. Haase, W. Saak, J. Stroot, S. Becke, J. Heinrichs .... 2056 – 2058

A Novel Route to Fulvene Complexes of Titanium—Diastereoselective Complexation of Pentafulvenes to Cyclopentadienyltitanium Fragments

Keywords: fulvene complexes · insertion · pi interactions · titanium

1433-7851/01/4011-1987 $ 17.50+.50/0

Modeling with paper clips? No, a general method for the fabrication of complex three-dimensional (3D) microstructures is reported. The 3D structure is decomposed into substructures that can be patterned onto separate substrates and then these substrustures are joined to form the desired microstructure. The picture shows an optical micrograph of a free-linked nickel chain mail.



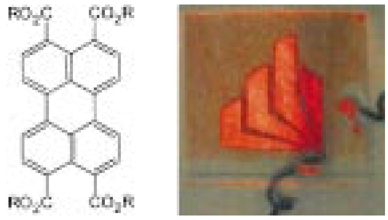
Angew. Chem. **2001**, *113*, 2115–2116

H. Wu, S. Whitesides,
G. M. Whitesides* 2059–2060

Fabrication of Micro-Chain Mail by Simultaneous, Patterned Electrodeposition on a Plane and Multiple Cylinders

Keywords: electrochemistry · lithography · microfabrication · patterning · topochemistry

Simple ester derivatives of polycyclic arenes offer access to light-emitting diodes of nearly any visible color by making use of the good charge-transport properties of the columnar liquid crystals of these derivatives. The picture shows the orange–red electroluminescence of a light-emitting diode containing the perylene 3,4,9,10-tetracarboxylic acid ethyl ester (structure shown, R = Et). Through use of multiple layers of different esters light-emitting diodes with almost white luminescence can be obtained.



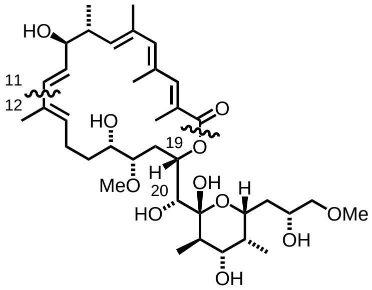
Angew. Chem. **2001**, *113*, 2119–2122

T. Hassheider, S. A. Benning,
H.-S. Kitzerow, M.-F. Achard,
H. Bock* 2060–2063

Color-Tuned Electroluminescence from Columnar Liquid Crystalline Alkyl Arenecarboxylates

Keywords: fluorescence · light-emitting diodes · liquid crystals · polycycles

A Cu^I-mediated coupling of the northern and southern units and a ring-size selective macrolactonization are the key steps in the convergent, first total synthesis of apoptolidinone, the aglycon of the potential antitumor compound apoptolidin. (The wavey lines in the picture are the retrosynthetic disconnections.)



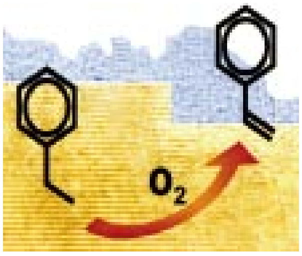
Angew. Chem. **2001**, *113*, 2125–2128

J. Schuppan, H. Wehlan, S. Keiper,
U. Koert* 2063–2066

Synthesis of Apoptolidinone

Keywords: apoptolidin · apoptosis · C–C coupling · natural products · total synthesis

Special carbon! Carbon nanofilaments differ from graphite and soot catalysts in their high stability during the oxidative dehydrogenation of ethylbenzene to styrene (see picture). The high yields of styrene achieved suggest that a first industrial application of carbon nanofilaments in catalysis is possible.



Angew. Chem. **2001**, *113*, 2122–2125

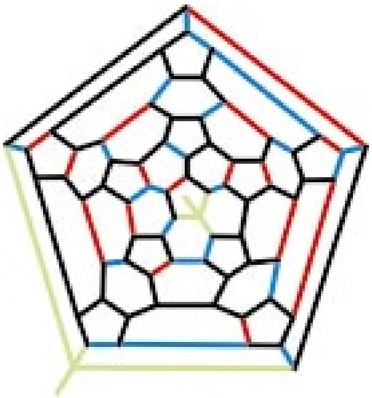
G. Mestl, N. I. Maksimova, N. Keller,
V. V. Roddatis, R. Schlögl* . 2066–2068

Carbon Nanofilaments in Heterogeneous Catalysis: An Industrial Application for New Carbon Materials?

Keywords: carbon · dehydrogenation · heterogeneous catalysis · nanofilaments

Under mild conditions, a linear polymeric $(C_{70}^{2-})_n$ fulleride was synthesized as single crystals which allow, for the first time, a complete structural analysis of a polymeric fulleride. Starting from the strongest "disturbance" of the cage geometry at the linkage sites, the pronounced alternation of the bond lengths decreases towards the middle of the C_{70} units (see Schlegel diagram of the C_{70}^{2-} building block; color coding of the bond lengths [Å]: blue <1.39, black 1.39–1.47, red 1.47–1.52 Å, green >1.52).

Angew. Chem. **2001**, *113*, 2117–2119



H. Brumm, E. Peters,
M. Jansen* 2069–2071

Linear Polymeric C_{70}^{2-} Ions

Keywords: anions • barium • fullerenes • polymers • solid-state chemistry

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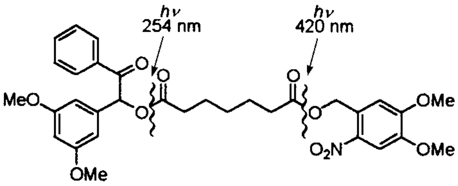
The selective activation of photolabile protecting groups was made possible by the use of monochromatic light of suitable wavelength. This new approach allowed the orthogonal deprotection of a substrate containing several photosensitive groups (see picture).

Angew. Chem. **2001**, *113*, 2140–2142



C. G. Bochet* 2071–2073

Orthogonal Photolysis of Protecting Groups

Keywords: chemoselectivity • chromophores • cleavage reactions • photochemistry • protecting groups

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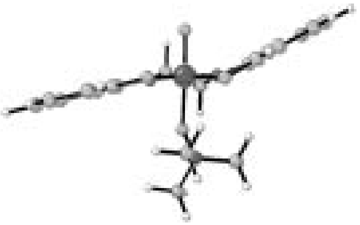
New light on the origin of the high enantioselectivities achieved in the Jacobsen–Katsuki epoxidation is shed by the results of density functional calculations. Axial ligation to the metal center not only enhances the epoxidation rate, but in addition leads to highly nonplanar, bent conformations of the active catalyst (see picture).

Angew. Chem. **2001**, *113*, 2131–2134



J. El-Bahraoui, O. Wiest,* D. Feichtinger,
D. A. Plattner* 2073–2076

Rate Enhancement and Enantioselectivity of the Jacobsen–Katsuki Epoxidation: The Significance of the Sixth Coordination Site

Keywords: density functional calculations • epoxidation • ligand effects • manganese • oxidation

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Synthetic ion channels containing δ-amino acids can become cation selective! δ-Amino acids with a cyclohexylether unit (see structure) were combined with structural motives from gramicidin A and led to channels with a NH_4^+/K^+ permeability ratio of $>10/1$. (The current trace for an NH_4^+ channel is shown.)

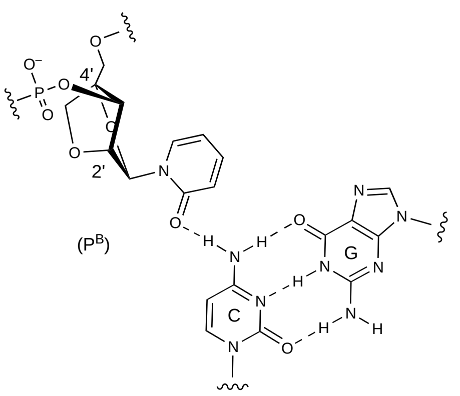
Angew. Chem. **2001**, *113*, 2137–2140

H.-D. Arndt, A. Knoll,
U. Koert* 2076–2078

Cyclohexylether δ-Amino Acids: New Leads for Selectivity Filters in Ion Channels

Keywords: amino acids • bioorganic chemistry • gramicidin A • ion channels • peptides

Significantly enhanced binding affinity to C · G base pairs without loss of sequence selectivity is achieved by using a nucleotide containing a 2-pyridone and a 2′-*O*,4′-*C*-methylene-bridged nucleic acid analogue (P^B, see picture). The degree of stabilization of the triplex formed enables C · G interruptions in a homopurine · homopyrimidine double-stranded DNA to be detected.



Angew. Chem. **2001**, *113*, 2149–2151

S. Obika, Y. Hari, M. Sekiguchi,
T. Imanishi* 2079–2081

A 2′,4′-Bridged Nucleic Acid Containing 2-Pyridone as a Nucleobase: Efficient Recognition of a C · G Interruption by Triplex Formation with a Pyrimidine Motif

Keywords: DNA recognition · nucleic acids · nucleobases · oligonucleotides

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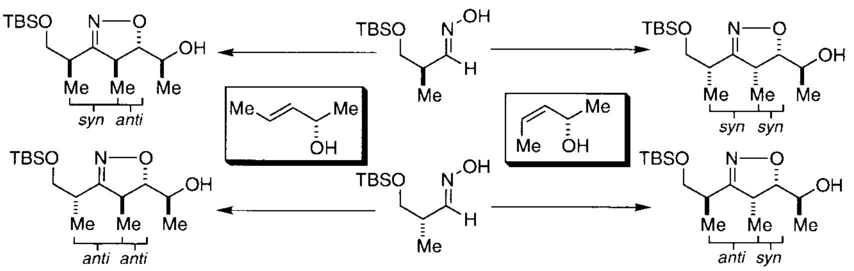
A single, convenient reaction protocol and the same set of readily available starting materials suffice for the modular synthesis of all possible polypropionate diastereomers (see scheme). This general method for the diastereoselective synthesis of *syn*, *anti*, and methyl ketone aldol adducts utilizes a powerful Mg^{II}-mediated, hydroxy-directed nitrile oxide cycloaddition. The free hydroxy group provides an ideal synthetic handle enabling the rapid assembly of complex polyketide structures. TBS = *t*BuMe$_2$Si.



Angew. Chem. **2001**, *113*, 2128–2131

J. W. Bode, N. Fraefel, D. Muri,
E. M. Carreira* 2082–2085

A General Solution to the Modular Synthesis of Polyketide Building Blocks by Kanemasa Hydroxy-Directed Nitrile Oxide Cycloadditions

Keywords: aldol reaction · cycloaddition · erythronolides · polyketides

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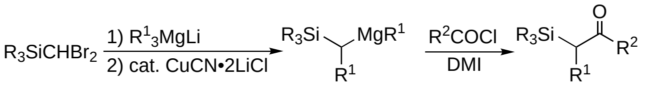
Magnesium – bromine exchange to provide the 1-bromo-1-silylmethylmagnesium species is mediated by treatment of dibromomethylsilane with an trialkylmagnesate reagent. The addition of a copper catalyst induces facile migration of an alkyl group to afford an α-silylalkylmagnesium compound, which furnishes α-silyl ketones in good yield upon treatment with acyl chloride (see scheme).



Angew. Chem. **2001**, *113*, 2146–2148

J. Kondo, A. Inoue, H. Shinokubo,
K. Oshima* 2085–2087

Alkylative Preparation of α-Silylalkylmagnesium from $R_3SiCHBr_2$ Using a Magnesate Reagent

Keywords: acylation · ate complexes · magnesium · metalation · silanes

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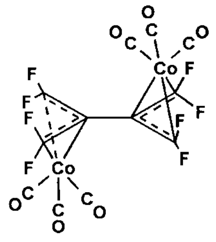
Cobalt and manganese complexes provide access to novel fluoroallyl ligands: Fluorinated bis(enyl) ligands can be easily synthesized by metal-induced dimerization of 1,1-difluoroallene and tetrafluoroallene. By using octacarbonyldicobalt the coupling reaction occurs at the central carbon atom of the allene leading to the formation of fluorinated μ-(η^3:η^3-2,3-dimethylenebuta-1,4-diyl) ligands such as those in complex **1**. Additional products arise from fluoride abstraction and CO insertion reactions. Decacarbonyldimanganese reacts with 1,1-difluoroallene under C–C coupling of the methylene group to give decacarbonyl-μ-(η^1:η^1-1,1,6,6-tetrafluoro-1,5-hexadiene-2,5-diyl)dimanganese.



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Angew. Chem. **2001**, *113*, 2142–2146

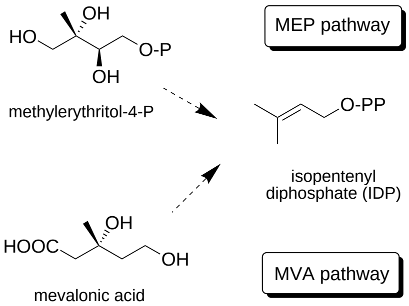
D. Lentz,* S. Willemsen 2087–2091

Fluorinated Bis(enyl) Ligands by Metal-Induced Dimerization of Fluorinated Allenes

Keywords: allenes · allyl complexes · carbonyl complexes · C–C coupling · dimerization

Plants utilize two different pathways for the biosynthesis of isopentenyl diphosphate, the universal building block of all terpenes (see scheme). Application of compound-specific isotope-ratio mass spectrometry (GC-C-IRMS) to volatile terpenoids allows distinction between the pathways on the basis of natural $^{12}C/^{13}C$ ratios.

Angew. Chem. **2001**, *113*, 2134–2137



A. Jux, G. Gleixner,
W. Boland* 2091–2094

Classification of Terpenoids according to the Methylerythritolphosphate or the Mevalonate Pathway with Natural $^{12}C/^{13}C$ Isotope Ratios: Dynamic Allocation of Resources in Induced Plants

Keywords: biosynthesis · isotope effects · mass spectrometry · terpenes

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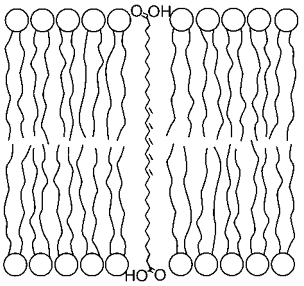
Inspired by *Archaebacterial* lipids, transmembrane probes anchor a sensing fluorescent polyene with Ångström resolution deep within a lipid layer (see figure). These new bolaamphiphiles are obtained in good yields from a double cross-coupling between esters with a terminal acetylene group and conjugated 1,ω-dihalopolyenes, followed by partial reduction of the triple bond.

Angew. Chem. **2001**, *113*, 2153–2155



E. Quesada, A. U. Acuña,*
F. Amat-Guerri* 2095–2097

New Transmembrane Polyene Bolaamphiphiles as Fluorescent Probes in Lipid Bilayers

Keywords: amphiphiles · fluorescence · lipids · membranes · polyenes

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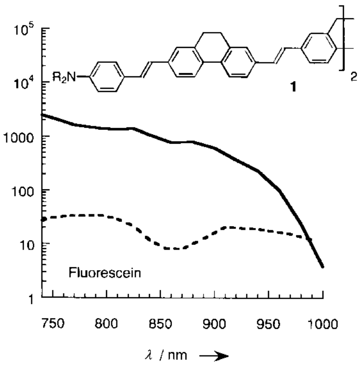
Outperforming fluorescein by far, elongated fluorophores (e.g. **1**) give rise to large two-photon absorption cross-sections σ_2 in the visible-red or NIR region and high quantum fluorescence yields Φ (see figure; GM = 10^{-50} cm^4 s photon^{-1}). This opens interesting prospects in the field of two-photon microscopy imaging of cell membranes.

Angew. Chem. **2001**, *113*, 2156–2159



L. Ventelon, S. Charier, L. Moreaux,
J. Mertz,
M. Blanchard-Desce* 2098–2101

Nanoscale Push–Push Dihydrophenanthrene Derivatives as Novel Fluorophores for Two-Photon-Excited Fluorescence

Keywords: chromophores · fluorescence · membranes · two-photon absorption · Wittig reactions

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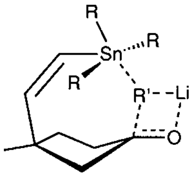
***syn* to tin** is the preferred mode of addition of organolithium reagents to the carbonyl group of cyclic ketones with a β-stannylvinyl group. This remarkable remote control is a consequence of the anchoring of the organolithium reagent by the tin and carbonyl groups (see picture).

Angew. Chem. **2001**, *113*, 2159–2161



A. Barbero, F. J. Pulido,* J. A. Rincón,
P. Cuadrado, D. Galisteo,
H. Martínez-García 2101–2103

Remote Stereocontrol in Carbonyl Additions Promoted by Vinylstannanes

Keywords: alkenes · cuprates · diastereoselectivity · ketones · tin

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Nitroaromatic explosives can be detected in a simple and rapid method by the quenching of the photoluminescence of fluorescent polysiloles. Quenching is achieved by electron transfer from the conduction band of the polysiloles to electron-poor molecules such as picric acid, nitrobenzene, 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT). Dilute polymer solutions can also be employed as a forensic spray-on reagent to visualize TNT or picric acid residues under a UV lamp (see picture of the print of a nitrile-gloved hand that had been in contact with TNT).

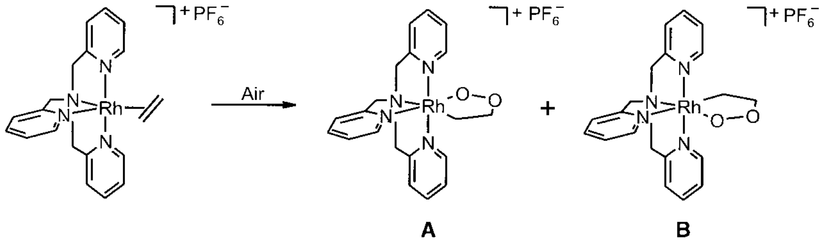
Angew. Chem. **2001**, *113*, 2162–2163

H. Sohn, R. M. Calhoun, M. J. Sailor,*
W. C. Trogler* 2104–2105

Detection of TNT and Picric Acid on Surfaces and in Seawater by Using Photoluminescent Polysiloles

Keywords: luminescence · nitroarenes · polymers · sensors · silicon

Proposed as intermediates in the catalytic oxidation of olefins to ketones, 3-rhoda-1,2-dioxolanes (κ^2C^1,O^2-2-peroxyethyl rhodium complexes) have now been prepared by oxygenation of *solid* [(N_4-ligand)Rh^I(ethene)]PF_6 (see scheme) with air. This process leads to stable isomeric 3-rhoda-1,2-dioxolanes **A** and **B**. Upon substitution of PF_6^- by BPh_4^- only isomer **B** is obtained. The X-ray structure of isomer **B** is presented.



Angew. Chem. **2001**, *113*, 2164–2166

M. Krom, R. G. E. Coumans,
J. M. M. Smits, A. W. Gal* 2106–2108

3-Rhoda-1,2-dioxolanes through Dioxygenation of a Rhodium–Ethene Complex by Air

Keywords: alkene complexes • metallacycles • N ligands • oxygenation • rhodium

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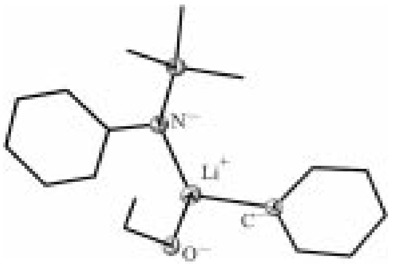
The three most important "superbase" anionic building blocks are contained in the striking decalithium aggregate in the structure of which a single lithium atom is surrounded solely by an amide, an alkoxide, and a carbanion (see picture).



Angew. Chem. **2001**, *113*, 2166–2169

P. C. Andrews, G. B. Deacon,*
C. M. Forsyth, N. M. Scott ... 2108–2111

A Striking, Multifaceted, Decalithium Aggregate with Carbanion, Organoamide, and Alkoxide Functionalities

Keywords: aggregation • alkoxides • amides • carbanions • lithium

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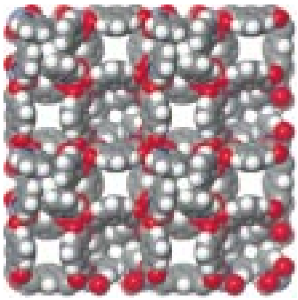
A series of bowls separated by hour-glass-shaped channels characterizes the structure of the undulating two-dimensional coordination polymer (see picture) that is prepared from a nanoscale secondary building unit (nSBU), which is formed by four square metal(II)carboxylate SBUs that have 1,3-benzenedicarboxylate units as 120° spacers.



Angew. Chem. **2001**, *113*, 2169–2171

S. A. Bourne, J. Lu, A. Mondal,
B. Moulton,
M. J. Zaworotko* 2111–2113

Self-Assembly of Nanometer-Scale Secondary Building Units into an Undulating Two-Dimensional Network with Two Types of Hydrophobic Cavity

Keywords: copper • crystal engineering • self-assembly • supramolecular chemistry • zinc

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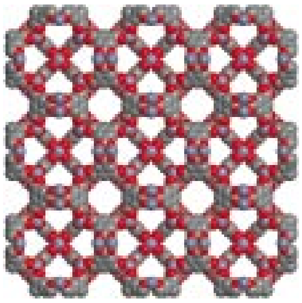
Small rhombihexahedra and small cubicuboctahedra (see picture), namely faceted polyhedra, form the basis of two novel low-density framework solids that are afforded by the self-assembly of molecular squares only or molecular squares and triangles, respectively.



Angew. Chem. **2001**, *113*, 2171–2174

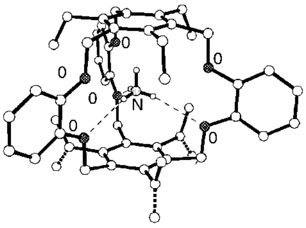
J. Lu, A. Mondal, B. Moulton,
M. J. Zaworotko* 2113–2116

Polygons and Faceted Polyhedra and Nanoporous Networks

Keywords: crystal engineering • networks • self-assembly • supramolecular chemistry • zinc

---

A cage-type receptor binds an NH_4^+ ion by cation–π interactions and hydrogen bonding (see picture) with high sensitivity and selectivity, comparable or even superior to those of the natural antibiotic nonactin over a wide pH range. The high performance, low cost, and easy synthesis may offer practical applications for this receptor as an ammonium ion sensor.



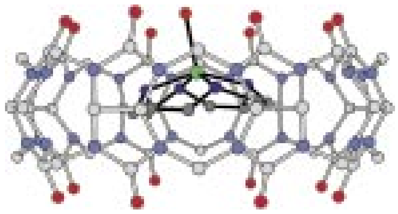
Angew. Chem. **2001**, *113*, 2174–2177

S. Y. Jon, J. Kim, M. Kim, S.-H. Park,
W. S. Jeon, J. Heo, K. Kim* . 2116–2119

A Rationally Designed NH_4^+ Receptor Based on Cation–π Interaction and Hydrogen Bonding

Keywords: ammonium ion • hydrogen bonds • molecular recognition • pi interactions • supramolecular chemistry

Reminiscent of Russian Matrioshka dolls, tetraazamacrocycles (1,4,7,10-tetraazacyclododecane (cyclen) and 1,4,8,11-tetraazacyclotetradecane (cyclam)) and their transition metal complexes are encapsulated in the cavity of cucurbit[8]uril (CB[8]). The X-ray crystal structure of the [Cu(cyclen)] in CB[8] complex (see picture; copper: green, oxygen: red, nitrogen: blue, carbon: gray) reveals a five-coordinate Cu^{II} center in a square-pyramidal environment with a water molecule bound to the axial position.



Angew. Chem. **2001**, *113*, 2177–2179

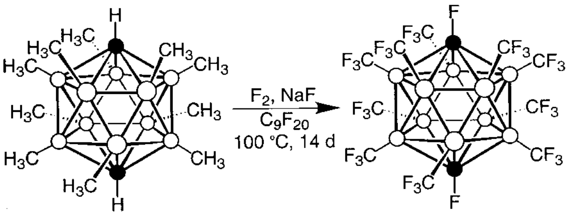
S.-Y. Kim, I.-S. Jung, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi, K. Kim* 2119–2121

Macrocycles within Macrocycles: Cyclen, Cyclam, and Their Transition Metal Complexes Encapsulated in Cucurbit[8]uril

Keywords: host–guest systems • macrocycles • solid-state structures • supramolecular chemistry • transition metals

---

Exhaustive fluorination of deca-*B*-methyl-*para*-carborane (**1**) furnishes perfluoro-deca-*B*-methyl-*para*-carborane (**2**) almost quantitatively [Eq. (1)]. Compound **2** represents the first neutral perfluorinated sphere mimicking a “Teflon ball”. The properties of **2** as well as its X-ray structure are discussed.



1 ○ = B ● = C **2**

(1)

Angew. Chem. **2001**, *113*, 2179–2181

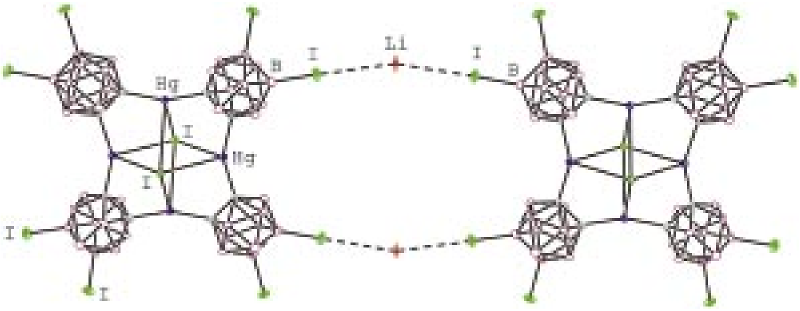
A. Herzog, R. P. Callahan, C. L. B. Macdonald, V. M. Lynch, M. F. Hawthorne,* R. J. Lagow* 2121–2123

A Perfluorinated Nanosphere: Synthesis and Structure of Perfluoro-deca-*B*-methyl-*para*-carborane

Keywords: carboranes • electron-deficient compounds • fluorine • Raman spectroscopy

---

Modular units of Li_2[*B*-octaiodo-12-mercuracarborand-4 · I_2] ($Li_2[(HgC_2B_{10}H_8I_2)_4 \cdot I_2]$) self-assemble forming infinite one-dimensional chains and microporous channels in the solid state (see picture). Self-assembly is directed by a unique B–I···Li···I–B intermolecular interaction involving electron-rich B–I vertices and electron-deficient lithium cations.



Angew. Chem. **2001**, *113*, 2182–2184

H. Lee, C. B. Knobler, M. F. Hawthorne* 2124–2126

Modular Self-Assembly of a Microporous Solid Based upon Mercuracarborand-4 and a New Bonding Motif

Keywords: carboranes • Lewis acids • macrocycles • microporosity • supramolecular chemistry

---

UV irradiation was found to accelerate the rate of gas incorporation into wide-bandgap ionic crystals and thus the rate of stoichiometry change. Up to now, this could only be achieved by changing the temperature, the dopant concentration, or adding catalytic coatings. The stoichiometry strongly affects the electrical conductivity of the crystal. The investigation of this effect provides valuable information on the mechanism of the surface reaction as well as offering new possible applications.

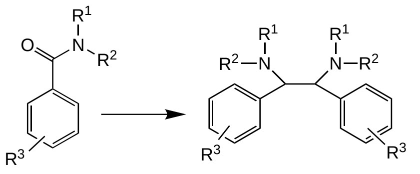
Angew. Chem. **2001**, *113*, 2184–2187

R. Merkle, R. A. De Souza, J. Maier* 2126–2129

Optically Tuning the Rate of Stoichiometry Changes: Surface-Controlled Oxygen Incorporation into Oxides under UV Irradiation

Keywords: kinetics • oxygen incorporation • semiconductors • surface chemistry • UV irradiation

A sequence of reduction, deoxygenation, and coupling steps results in a remarkable reaction, which represents an important new method for the synthesis of 1,2-diamines. The vicinal diamines are formed by the facile coupling of aromatic amides in the presence of titanocene catalysts and $PhMeSiH_2$ (see scheme).



Angew. Chem. **2001**, *113*, 2187–2189

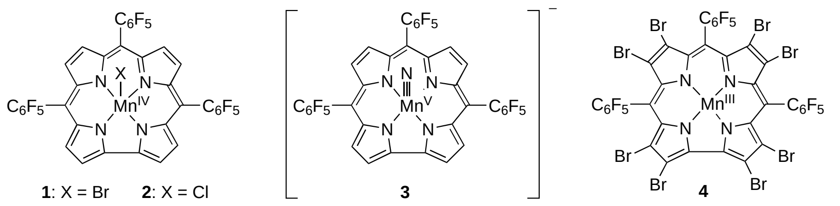
K. Selvakumar, J. F. Harrod* 2129–2131

Titanocene-Catalyzed Coupling of Amides in the Presence of Organosilanes To Form Vicinal Diamines

Keywords: amides · diamines · homogeneous catalysis · silanes · titanium

---

On pyrrole! The pyrrole-based corrole ligands can offer an alternative to porphyrin systems. The manganese corroles **1**–**4** are readily synthesized, undergo metal- not ligand-based redox chemistry, and **4** in particular shows impressive catalytic activity in the oxygenation of styrene with iodosylbenzene.



1: X = Br **2**: X = Cl **3** **4**

Angew. Chem. **2001**, *113*, 2190–2192

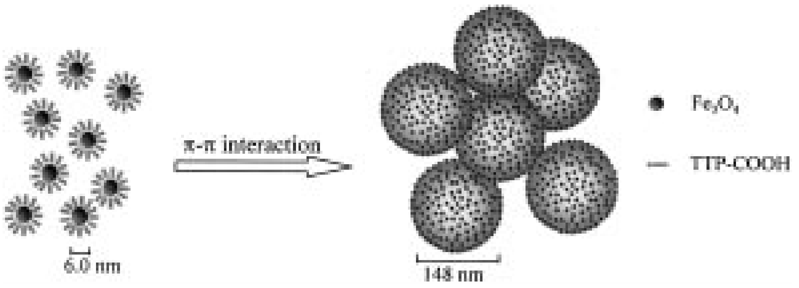
G. Golubkov, J. Bendix, H. B. Gray,*
A. Mahammed, I. Goldberg,*
A. J. DiBilio, Z. Gross* 2132–2134

High-Valent Manganese Corroles and the First Perhalogenated Metallocorrole Catalyst

Keywords: corroles · epoxidation · homogeneous catalysis · manganese · porphyrinoids

---

Nanoparticles of Fe_3O_4 coated with 2-carboxyterthiophene (TTP-COOH) self-assemble through π–π interactions to form uniform transparent microspheres (see schematic representation). The interaction between individual particles is relatively weak and the spherical aggregates can be destroyed by sonication to leave the monodispersed nanoparticles.



Angew. Chem. **2001**, *113*, 2193–2196

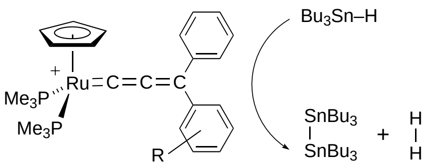
J. Jin, T. Iyoda, C. Cao, Y. Song,
L. Jiang,* T. J. Li,*
D. B. Zhu 2135–2138

Self-Assembly of Uniform Spherical Aggregates of Magnetic Nanoparticles through π–π Interactions

Keywords: aggregation · magnetic properties · nanoparticles · pi interactions · self-assembly

---

Conjuring with conjugation: catalysis by ruthenium–allenylidene complexes has been observed for the conversion of tin hydrides into distannanes and dihydrogen (see scheme). Alkyne or alkene groups (R) in conjugation with an aromatic ring are required for catalytic activity, providing an unusual example of control of metal-centered reactivity by a remote substituent.



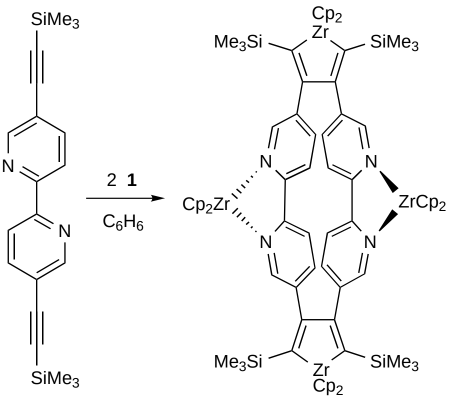
Angew. Chem. **2001**, *113*, 2196–2199

S. M. Maddock, M. G. Finn* 2138–2141

Dehydrogenative Dimerization of Tin Hydrides Catalyzed by Ruthenium–Allenylidene Complexes

Keywords: allenylidene complexes · dehydrogenation · homogeneous catalysis · ruthenium · tin

A zirconocene double act: The course of zirconocene-mediated macrocyclization is controlled by templating effects. In macrocyclizations of bipyridine-containing diynes, the zirconocene reagent $[Cp_2Zr(py)(Me_3SiC{\equiv}SiMe_3)]$ (**1**; py = pyridine) acts as both coupling and templating agent. Thus, by controlling the stoichiometry, dimeric (see scheme) or trimeric macrocycles are obtained.



Angew. Chem. **2001**, *113*, 2200–2203

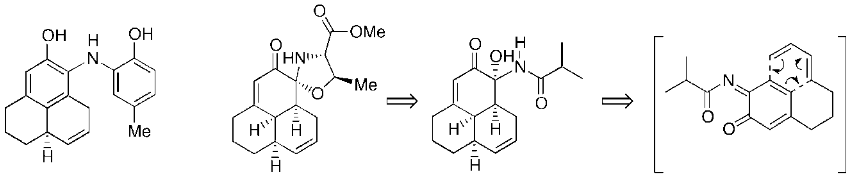
J. R. Nitschke, T. D. Tilley* . 2142–2145

Novel Templating Effect in the Macrocyclization of Functionalized Diynes by Zirconocene Coupling

Keywords: cyclodimerization · cyclotrimerization · macrocycles · template synthesis · zirconium

---

A multitude of natural product like molecules such as **2** and **3** can be readily obtained from hydroxyketoamide **1**. The versatile **1** is derived, via the intermediate *o*-azaquinone **4**, from the Dess–Martin periodinane oxidation of the corresponding anilide.



2 3 1 4

Angew. Chem. **2001**, *113*, 2203–2207

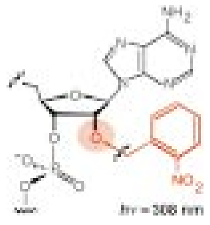
K. C. Nicolaou,* Y.-L. Zhong, P. S. Baran, K. Sugita 2145–2149

Rapid Access to Complex Molecular Architectures via *o*-Azaquinones

Keywords: azaquinones · cycloaddition · domino reactions · oxidation · synthetic methods

---

Getting spliced? Pre-mRNA splicing is catalyzed by the spliceosome, a complex assembly of proteins and RNA, which forms in an ordered fashion on the substrate. If one of the residues of the substrate is caged with a photolabile *o*-nitrobenzyl group, the splicing reaction can be transiently blocked, until subsequent initiation by photolysis of the complexes (see scheme). This RNA-caging approach effectively separates the spliceosome assembly from the catalytic reaction and allows the two processes to be studied independently.



Angew. Chem. **2001**, *113*, 2207–2210

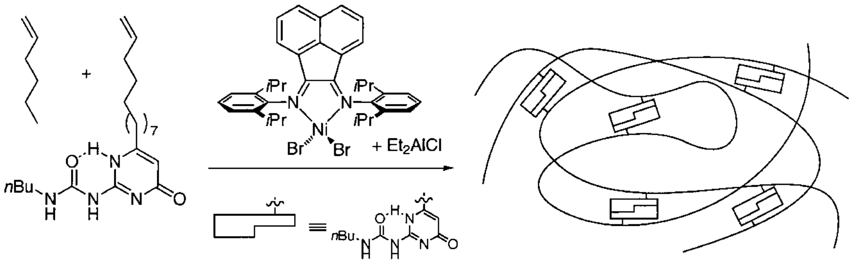
S. G. Chaulk, A. M. MacMillan* 2149–2152

Separation of Spliceosome Assembly from Catalysis with Caged pre-mRNA Substrates

Keywords: mRNA · photolysis · protein–RNA interactions · splicing

---

Mimicking nature: The central mechanisms of living organisms depend on the formation of specific hydrogen bonds. Advances in the areas of catalysis and supramolecular chemistry have been applied here for the synthesis of a novel class of elastomeric polyolefins (see scheme) with properties dependent upon strong intermolecular hydrogen bonding.



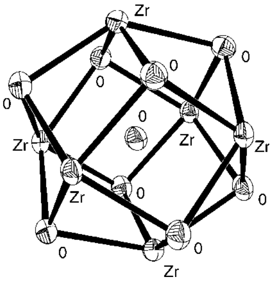
Angew. Chem. **2001**, *113*, 2211–2214

L. R. Rieth, R. F. Eaton, G. W. Coates* 2153–2156

Polymerization of Ureidopyrimidinone-Functionalized Olefins by Using Late-Transition Metal Ziegler–Natta Catalysts: Synthesis of Thermoplastic Elastomeric Polyolefins

Keywords: homogeneous catalysis · hydrogen bonds · polymerization · self-assembly · supramolecular chemistry

KH and the two-phase system liquid ammonia/toluene provide the basis for a new method for the synthesis of organozirconium oxides such as $[\{(EtMe_4C_5)Zr\}_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]\cdot C_7H_8$ (the central inorganic core of the cluster is shown). Altering the solvent to mesitylene has no influence on the core structure of the resulting organozirconium oxide.



Angew. Chem. **2001**, *113*, 2214–2217

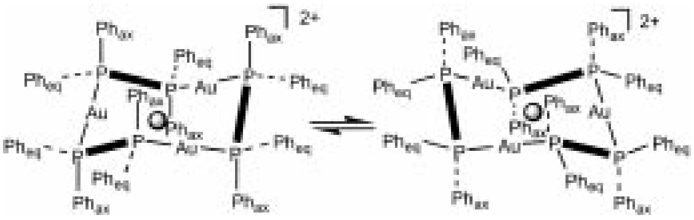
G. Bai, H. W. Roesky,* P. Lobinger,
M. Noltemeyer,
H.-G. Schmidt 2156–2159

Base-Assisted Formation of Organozirconium Oxides with the $[Zr_6(\mu_6\text{-}O)(\mu_3\text{-}O)_8]$ Core Structure

Keywords: ammonia · cluster compounds · hydrolysis · oxides · zirconium

---

A chair of gold: Analogous to cyclohexane, the trinuclear gold ring $[Au_3(PAnP)_3][ClO_4]_3$ (PAnP = 9,10-bis(diphenylphosphino)anthracene) shows a chair conformation and diastereotopic axial and equatorial phenyl rings. Variable temperature and 2D EXSY NMR studies reveal that the gold ring undergoes cyclohexane-like ring inversion (enantiomerization) in solution. In addition, the gold ring exhibits intense excimeric emission at room temperature. ▬ = anthracene ring system in PAnP, ● = ClO_4^-.



Angew. Chem. **2001**, *113*, 2217–2220

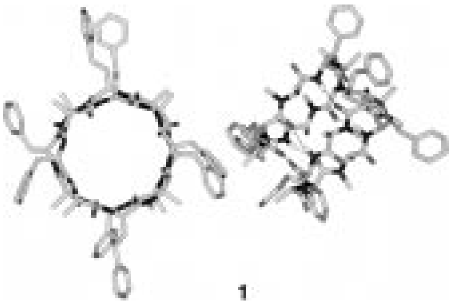
J. H. K. Yip,* J. Prabhavathy 2159–2162

A Luminescent Gold Ring That Flips Like Cyclohexane

Keywords: conformations · fluxionality · gold · luminescence · NMR spectroscopy

---

A supramolecular recognition interface is formed through the self-assembly of cyclic D,L-peptides. Phenyl–phenyl interactions direct the solid-state organization of dimeric peptide *cyclo*[(-L-Phe-D-^{Me}*N*-Ala-L-hPhe-D-^{Me}*N*-Ala)$_2$] (**1**) by forming clusters of edge-to-face contacts between dimers (shown left), which suggests that these peptide scaffolds may be useful subunits for crystal engineering.



1

Angew. Chem. **2001**, *113*, 2221–2224

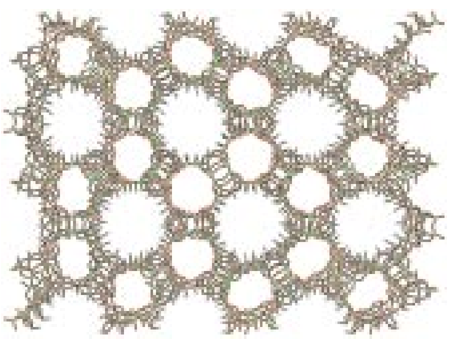
D. T. Bong, M. R. Ghadiri* 2163–2166

Self-Assembling Cyclic Peptide Cylinders as Nuclei for Crystal Engineering

Keywords: crystal engineering · nanostructures · peptides · pi interactions · self-assembly

---

Pores for thought: A new extra large germanate zeolite-type structure has been synthesized by using high-charge multiamine as a template in a pseudo-aqueous system (DMF/H_2O). The novel zeolite-type germanate with low framework density (11.1) has a 24- and 12-membered ring honeycomb array (see picture) with three-dimensional intersecting channels.



Angew. Chem. **2001**, *113*, 2224–2226

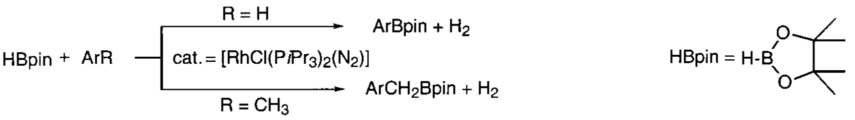
Y. Zhou, H. Zhu, Z. Chen, M. Chen,
Y. Xu, H. Zhang, D. Zhao* 2166–2168

A Large 24-Membered-Ring Germanate Zeolite-Type Open-Framework Structure with Three-Dimensional Intersecting Channels

Keywords: germanium · microporosity · template synthesis · zeolite analogues

1433-7851/01/4011-1996 $ 17.50+.50/0

Direct borylation of C–H bonds in aromatic compounds can be achieved by using the efficient homogeneous catalyst precursor [RhCl(P*i*Pr$_3$)$_2$(N$_2$)] and pinacolborane (HBpin; see scheme). High selectivity for the benzyl positions, observed for toluene, *p*-xylene, and mesitylene, was attributed to the formation of η^3-benzyl intermediates.



Angew. Chem. **2001**, *113*, 2226–2229

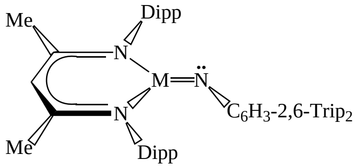
S. Shimada, A. S. Batsanov,
J. A. K. Howard,
T. B. Marder* 2168–2171

Formation of Aryl- and Benzylboronate Esters by Rhodium-Catalyzed C–H Bond Functionalization with Pinacolborane

Keywords: boron · C–H activation · homogeneous catalysis · phosphanes · rhodium

---

A short Ga–N bond with double-bond character is displayed by the first monomeric imide of gallium, which was obtained by the reaction of [{HC(MeCDippN)$_2$}M:] (Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$, M = Ga; see picture) with N$_3$-2,6-Trip$_2$C$_6$H$_3$ (Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$). The analogous aluminum (M = Al) compound is also readily available.



Angew. Chem. **2001**, *113*, 2230–2232

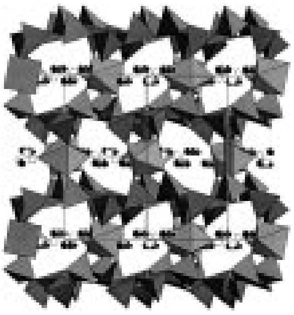
N. J. Hardman, C. Cui, H. W. Roesky,
W. H. Fink, P. P. Power* 2172–2174

Stable, Monomeric Imides of Aluminum and Gallium: Synthesis and Characterization of [{HC(MeCDippN)$_2$}MN-2,6-Trip$_2$C$_6$H$_3$] (M = Al or Ga; Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$; Trip = 2,4,6-*i*Pr$_3$C$_6$H$_2$)

Keywords: aluminum · β-ketiminates · gallium · imides · multiple bonds · terphenyls

---

Silicate layers cross-linked by interlayer VO$_5$ square pyramids form the basis of the three-dimensional frameworks of the structures of the title compounds (the structure of K$_2$(VO)(Si$_4$O$_{10}$) · H$_2$O is depicted). Alkali metal cations (●) and water molecules (○) occupy nonframework sites in these structures, which were synthesized hydrothermally.



Angew. Chem. **2001**, *113*, 2232–2234

X. Wang, L. Liu,
A. J. Jacobson* 2174–2176

The Novel Open-Framework Vanadium Silicates K$_2$(VO)(Si$_4$O$_{10}$) · H$_2$O (VSH-1) and Cs$_2$(VO)(Si$_6$O$_{14}$) · 3 H$_2$O (VSH-2)

Keywords: hydrothermal synthesis · silicates · solid-state structures · vanadium

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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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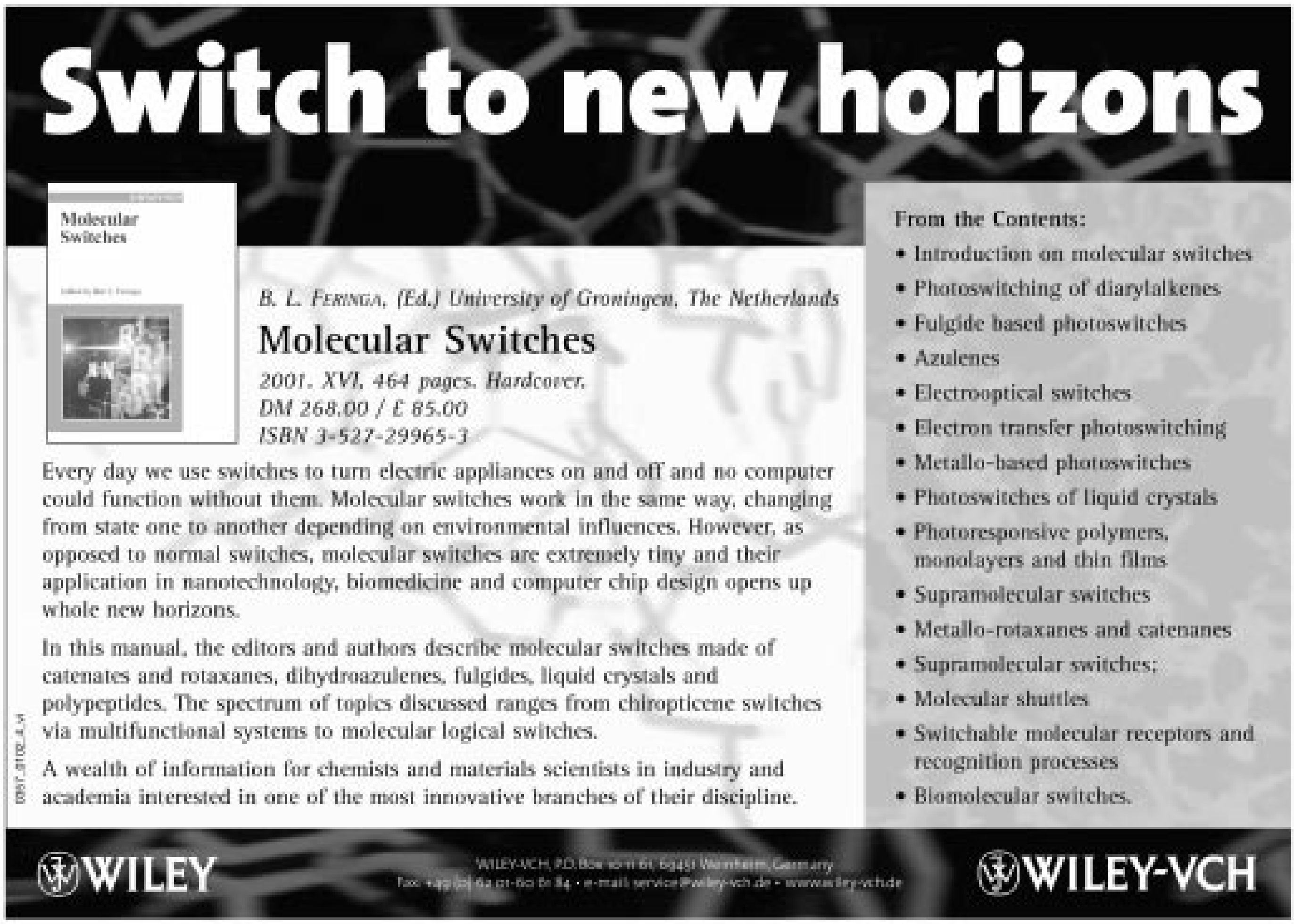

Switch to new horizons

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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