ANGEWANDTE CHEMIE

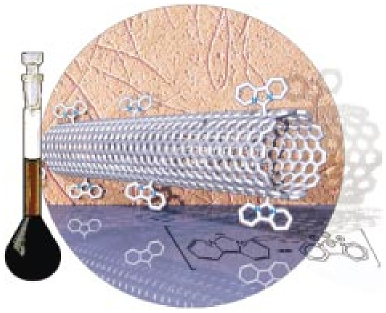
A Journal of the
Gesellschaft
Deutscher Chemiker

INTERNATIONAL EDITION

2001
40/21
Pages 3927–4108

COVER PICTURE

The cover picture shows a single-walled carbon nanotube (SWNT) functionalized with nucleophilic carbenes at the sidewall. Normally, single-walled nanotubes exist in the form of insoluble bundles. The sidewall addition of reactive organic groups such as radicals, nitrenes, or carbenes such as the ones shown in the cover picture disrupts the bundles. The background of the picture shows a typical AFM image of such derivatized SWNTs. The isolated SWNTs are soluble in organic solvents giving black solutions. This enables a spectroscopic characterization of nanotubes in solution. With this versatile sidewall functionalization the decisive requirements for the development of technological applications such as the production of ultrathin films or the processing to polymer composites with new electronic and mechanic properties have been compiled. Details about this new chemical funtionalization of SWNTs is described by Hirsch et al. on pp. 4002 ff.

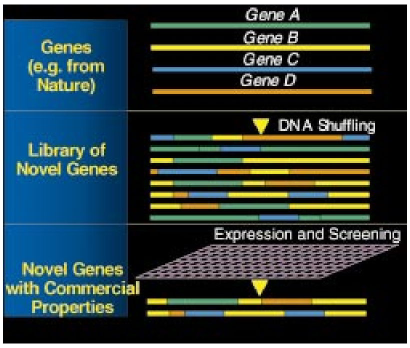


REVIEWS

Contents

Advances in directed molecular evolution are now having an impact on the field of biocatalysis. One can envision biocatalytic processes in which the enzyme has been designed to operate under optimal process conditions (see picture), instead of processes in which the conditions have been constrained to accommodate the enzyme.

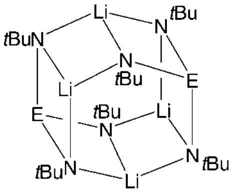
Angew. Chem. **2001**, *113*, 4068–4080



K. A. Powell,* S. W. Ramer,
S. B. delCardayré, W. P. C. Stemmer,
M. B. Tobin, P. F. Longchamp,
G. W. Huisman 3948–3959

Directed Evolution and Biocatalysis

Keywords: directed evolution · DNA shuffling · enzyme catalysis · enzyme libraries · proteins



The full or partial replacement of oxygen in salts of common oxo anions by imido (NR) groups generates a new class of polycyclic compounds. These ternary or quaternary clusters adopt structures derived from the aggregation of the simple building blocks formed by binary imido systems. The appropriate choice of NR groups may allow the production of functional materials with specific applications. These anions are also attracting attention as multidentate ligands with unusual electronic and stereochemical characteristics that may lead to new metal-centered chemistry. In the ternary cluster shown, E = S, Se, Te.

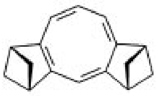
Angew. Chem. **2001**, *113*, 4082–4098

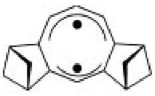
J. K. Brask, T. Chivers* 3960–3976

Imido Analogues of Common Oxo Anions: A New Episode in the Chemistry of Cluster Compounds

Keywords: cluster compounds · coordination modes · isoelectronic analogues · main group elements · transition metals

MINIREVIEW


1


1'

A negligible antiaromatic destabilization is found in planar D_{4h} 1,3,5,7-cyclooctatetraene with alternating bond lengths. The same is also true for the delocalized D_{8h} structure, which has a stabilization energy of only 3–4 kcal mol^{-1}. According to quantum-chemical calculations, the ground state of **1** is expected to be the planar C_{2v}-symmetric (1,1) singlet diradical **1'**.

Angew. Chem. **2001**, *113*, 4099–4103

F.-G. Klärner* 3977–3981

About the Antiaromaticity of Planar Cyclooctatetraene

Keywords: antiaromaticity · cyclooctatetraene · diradicals · resonance energy

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

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

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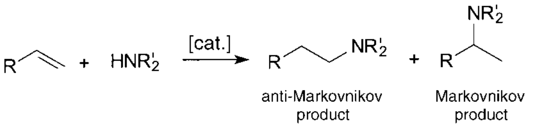
1433-7851/01/4021-3930 $ 17.50+.50/0

HIGHLIGHT

In terms of an optimum material balance, intermolecular catalytic hydroamination reactions [Eq. (1)] are one of the much discussed atom-economical processes. The problems of hydroamination have not yet been properly solved; however, recent publications describe some very promising work on the homogeneous catalysis of intermolecular hydroamination reactions with transition metal catalysts. This work is described and discussed herein.



(1)

Angew. Chem. **2001**, *113*, 4105–4108

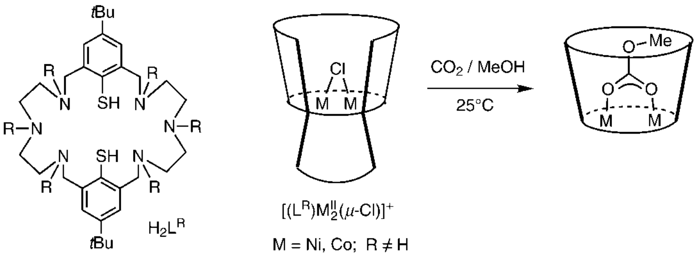
M. Nobis,
B. Driessen-Hölscher* 3983–3985

Recent Developments in Transition Metal Catalyzed Intermolecular Hydroamination Reactions—A Breakthrough?

Keywords: density functional calculations · homogeneous catalysis · hydroamination · transition metal catalysis

COMMUNICATIONS

The unusual reactivity of binuclear complexes of the macrocyclic ligand $(L^R)^{2-}$ can be attributed to the hydrophobic microenvironment about the free coordination site. The new compounds can be used for the stabilization of reactive intermediates or for the activation of small molecules such as carbon dioxide (see scheme).



Angew. Chem. **2001**, *113*, 4109–4112

B. Kersting* 3987–3990

Carbon Dioxide Fixation by Binuclear Complexes with Hydrophobic Binding Pockets

Keywords: binuclear complexes · carbon dioxide fixation · hydrophobic effect · ligand effects · macrocyclic ligands

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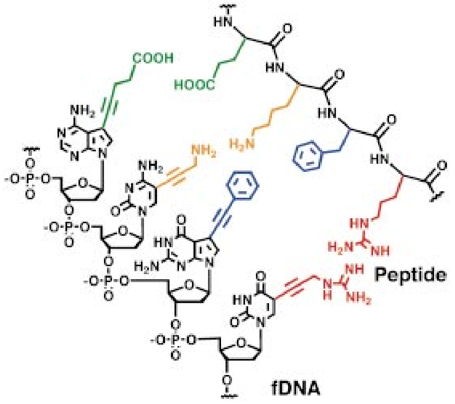
New DNA: By enzymatic polymerization of base-modified nucleoside triphosphates, a functionalized DNA (fDNA; see picture) was generated in which every base bears an additional amino acid like residue, thus mimicking the functional group repertoire of peptides on a nucleic acid backbone. These modified oligonucleotides can in turn serve as templates for polymerase chain reaction amplification, thus utilizing fDNA as a novel class of biopolymers for in vitro selection techniques.



Angew. Chem. **2001**, *113*, 4112–4115

O. Thum, S. Jäger,
M. Famulok* 3990–3993

Functionalized DNA: A New Replicable Biopolymer

Keywords: combinatorial chemistry · in vitro selection · nucleotides · oligonucleotides

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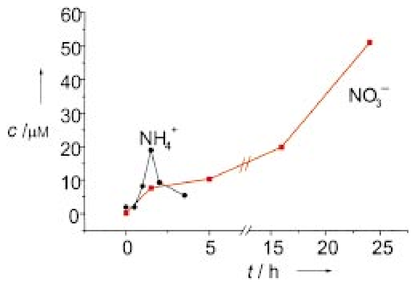
Mild reducing agents such as ethanol, sodium formate, and humic acids effect the photofixation of nitrogen to ammonia and nitrate at thin films of nanostructured iron titanates (see diagram). The reaction occurs in the presence of air and light, but is inhibited by the presence of carbon monoxide.



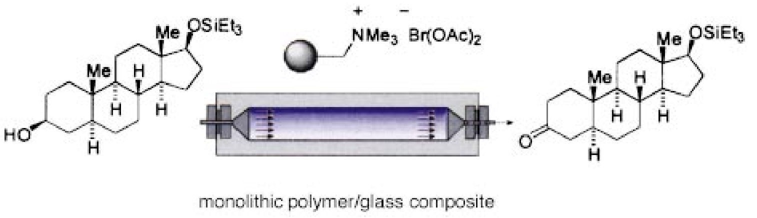
Angew. Chem. **2001**, *113*, 4115–4117

O. Rusina, A. Eremenko, G. Frank,
H. P. Strunk, H. Kisch* 3993–3995

Nitrogen Photofixation at Nanostructured Iron Titanate Films

Keywords: iron · nanocrystals · nitrogen fixation · photochemistry · thin films · titanium

A chemist's wish finally becomes reality: microreactors for every synthetic laboratory! By precipitation polymerization various polymers are introduced into the irregular pore system of a porous glass rod. By embedding these rods into a housing, followed by functionalization and immobilization of reagents onto the polymer phase, versatile microreactors are obtained. With this apparatus, chemical transformations in solution can be performed, for example, a steroid derivatization (see picture).



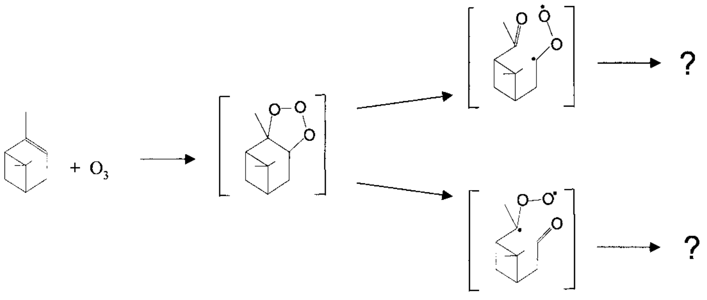
Angew. Chem. **2001**, *113*, 4118–4120

A. Kirschning,* C. Altwicker, G. Dräger, J. Harders, N. Hoffmann, U. Hoffmann, H. Schönfeld, W. Solodenko, U. Kunz* 3995–3998

PASSflow Syntheses Using Functionalized Monolithic Polymer/Glass Composites in Flow-Through Microreactors

Keywords: immobilization · microreactor · polymerization · solid-phase syntheses · synthetic methods

Unknown products identified precisely: The coupling of liquid chromatography to NMR spectroscopy, mass spectrometry, and infrared spectroscopy and the use of high-resolution mass spectrometry is utilized to investigate the formation of atmospheric-relevant organic aerosols. The investigation focussed on the gas-phase reaction of α-pinene with ozone (see scheme) and the subsequent identification of the reaction products by the coupled analytical techniques.



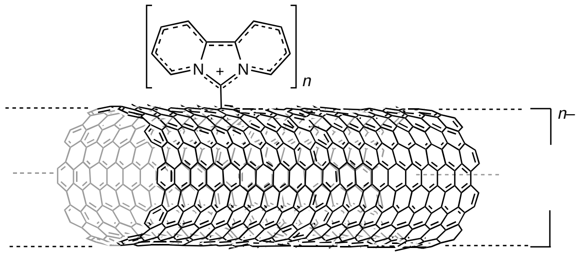
Angew. Chem. **2001**, *113*, 4129–4132

W. Schrader,* J. Geiger, M. Godejohann, B. Warscheid, T. Hoffmann 3998–4001

An Analytical Approach for a Comprehensive Study of Organic Aerosols

Keywords: analytical methods · atmospheric chemistry · liquid chromatography · terpenoids

The addition of nitrenes, nucleophilic carbenes, and radicals affords soluble, individual single-walled nanotubes (shown here is a carbene-functionalized adduct) by covalent sidewall functionalization. The characterization, a fundamental problem in nanotube chemistry, is simple to carry out.

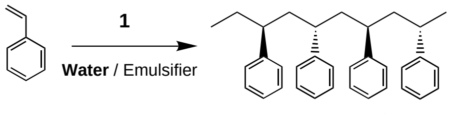


Angew. Chem. **2001**, *113*, 4132–4136

M. Holzinger, O. Vostrowsky, A. Hirsch,* F. Hennrich, M. Kappes, R. Weiss, F. Jellen 4002–4005

Sidewall Functionalization of Carbon Nanotubes

Keywords: carbenes · carbon allotropes · cycloaddition · nanotubes · nitrenes



Water-sensitive catalysts work in water! Metallocene catalysts that normally have to be handled under the strict exclusion of air and moisture, for example [TiCp*(OMe)$_3$] (**1**, Cp* = pentamethylcyclopentadienyl), are successfully employed in the aqueous emulsion polymerization of styrene to syndiotactic polystyrene. The catalyst is encapsulated inside the monomer droplets and thus protected against attack by water.

Angew. Chem. **2001**, *113*, 4139–4141

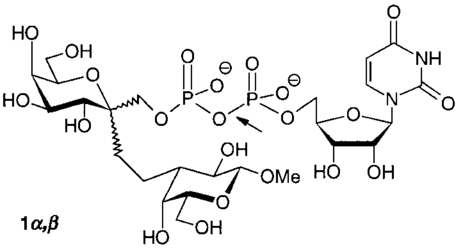
B. Manders,* L. Sciandrone, G. Hauck, M. O. Kristen* 4006–4007

No Polymerization with Metallocenes in Water?—A Prejudice is Refuted

Keywords: homogeneous catalysis · metallocenes · polymerization · polystyrene · titanium

How do retaining glycosyltransferases function? To answer this question, UDP-Gal and galactose were covalently linked to form disubstrate analogues **1**, of which surprisingly **1β** and not **1α** inhibited α(1-3)-galactosyltransferases very well. An understanding of this inhibition is a key to the pharmacological prevention of hyperacute rejection in pig to primate xenotransplantation.

Angew. Chem. **2001**, *113*, 4120–4124



1α,β

B. Waldscheck, M. Streiff, W. Notz,
W. Kinzy, R. R. Schmidt* ... 4007–4011

α(1-3)-Galactosyltransferase Inhibition Based on a New Type of Disubstrate Analogue

Keywords: C-glycosides · C-ketosides · disubstrate analogues · inhibitors · transferases

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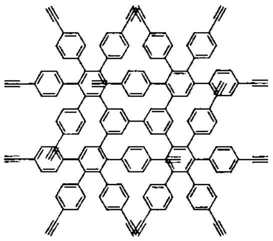
Rigid, **dendritic poly(paraphenylene)s** (see picture) are excellently suited as sensitive and selective coatings for gravimetric sensors (quartz microbalances), since they incorporate guest molecules reversibly into their interior voids. The variety of their potential designs allows an optimal match of these multitalented hosts to the guests (analytes) to be monitored.

Angew. Chem. **2001**, *113*, 4124–4129



M. Schlupp,* T. Weil, A. J. Berresheim,
U. M. Wiesler, J. Bargon,*
K. Müllen* 4011–4015

Polyphenylene Dendrimers as Sensitive and Selective Sensor Layers

Keywords: dendrimers · host–guest chemistry · polyphenylene · quartz microbalance · sensors

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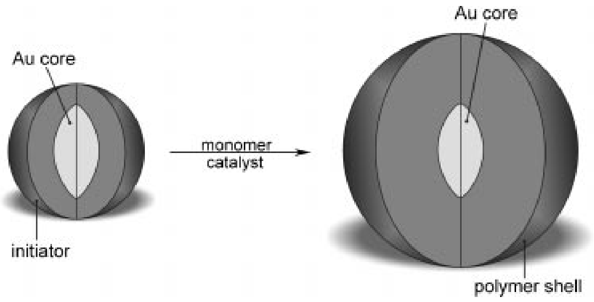
"Living"/controlled radical polymerization according to the atom transfer radical polymerization mechanism is a suitable method for the graft-polymerization of nanoparticles (see scheme). With this method, in which the core nanoparticles remain unchanged, the chain length and therefore the thickness of the polymer shell can be adjusted.



Angew. Chem. **2001**, *113*, 4137–4139

S. Nuß, H. Böttcher, H. Wurm,
M. L. Hallensleben* 4016–4018

Gold Nanoparticles with Covalently Attached Polymer Chains

Keywords: colloids · gold · nanostructures · organic–inorganic hybrid composites · polymers

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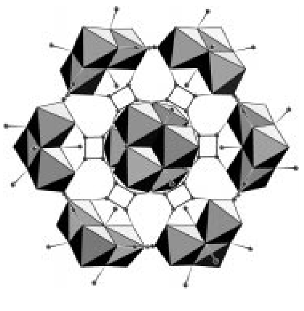
Polydentate bridging ligands can be used to link small polyoxo-alkoxo-metalate units to form supramolecular clusters. In the title compound, twelve μ_4-bridging squarato groups connect eight trinuclear methoxo-oxo-vanadate units to form a tetradodecanuclear cubic framework (see picture), in whose cavity six *n*-butyl groups of the tetra-*n*-butylammonium cations are anchored.

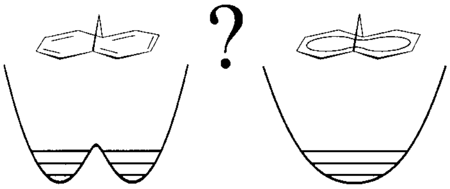
Angew. Chem. **2001**, *113*, 4141–4143



J. Spandl, I. Brüdgam,
H. Hartl* 4018–4020

Solvothermal Synthesis of a 24-Nuclear, Cube-Shaped Squarato-oxovanadium(IV) Framework: $[N(n\mathrm{Bu})_4]_8[V_{24}O_{24}(C_4O_4)_{12}(OCH_3)_{32}]$

Keywords: cage compounds · polyoxometalates · solvothermal synthesis · squarates · structure elucidation · vanadium



For the ground state of the Hückel aromatic ring 1,6-methano[10]annulene (MA) both a localized and a delocalized structure (see scheme) have been proposed in the past, depending on the theoretical methods used. A high-resolution electronic spectrum in a supersonic jet unambiguously shows that isolated, ultracold MA has a delocalized structure in its S_0 ground state as well as in its S_1 excited state.

Angew. Chem. **2001**, *113*, 4144–4146

R. Seiler, B. Dick* 4020–4023

1,6-Methano[10]annulene has a Delocalized Structure in S_0 and S_1: High-Resolution Spectroscopy in a Supersonic Jet

Keywords: aromaticity · delocalization · laser spectroscopy · VB methods

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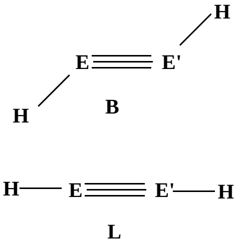
Bond stabilization through bending! Valence bond analysis shows that the σ frames of **1**–**3** (**1**: E = Si, E′ = C; **2**: E = E′ = Si; **3**: E = E′ = C) are stabilized by *trans* bending (**B**), while π bonding is weakened. In acetylene (**3**) π bonding overrides the σ frame and establishes a linear molecule (**3L**). In contrast, the σ frames dominate in silyne (**1**) and disilyne (**2**) and lead to *trans*-bent structures (**1B** and **2B**).



Angew. Chem. **2001**, *113*, 4146–4150

D. Danovich, F. Ogliaro, M. Karni, Y. Apeloig,* D. L. Cooper,* S. Shaik* 4023–4026

Silynes (RC≡SiR′) and Disilynes (RSi≡SiR′): Why Are Less Bonds Worth Energetically More?

Keywords: bond theory · multiple bonds · silicon · valence bond calculations

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Really a triple bond? According to quantum-chemical calculations of inverted Hessian matrices (compliance matrices), the strength of the C≡Si bond in **I** is only marginally stronger than the C=Si bond in silaethylene (**II**). Real-space force constants overestimate the C≡Si bond in **I** and should therefore be abandoned as bond strength descriptors.

Angew. Chem. **2001**, *113*, 4150–4153

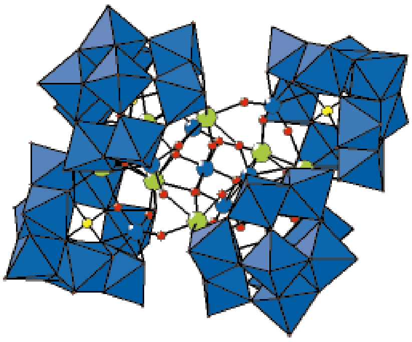
J. Grunenberg* 4027–4029

Intrinsic Bond Strengths of Multiple C–C, Si–Si, and C–Si Bonds

Keywords: ab initio calculations · bond theory · density functional calculations · multiple bonds · silicon

---

Four lacunary $PW_9O_{34}^{9-}$ ions (blue polyhedra) are held together by eight M^{III} (M = Y, Eu) ions and seven W atoms that form a $[M_8W_7O_{30}]^{6+}$ network (center) in the novel heteropolyoxometalates $[(PM_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$. In the solid state, the anions interact strongly with K^+ countercations, which thus play a role in the formation of this particular structure.



Angew. Chem. **2001**, *113*, 4155–4158

R. C. Howell, F. G. Perez, S. Jain, W. DeW. Horrocks, Jr., A. L. Rheingold, L. C. Francesconi* 4031–4034

A New Type of Heteropolyoxometalates formed from Lacunary Polyoxotungstate Ions and Europium or Yttrium Cations

Keywords: europium · lanthanides · polyoxometalates · tungsten · yttrium

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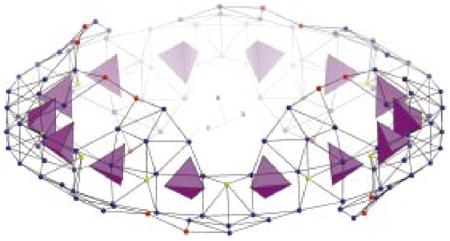

Are adaptations in the nanocosmos observable? Or in other words, can formation or self-assembly of nanoparticles be achieved with a variety of characteristic modifications of a parent structure based solely on the variation of boundary conditions? This possibility exists for the ring-shaped nanostructured giant molybdenum clusters—known as "big wheels" (see picture)—in which well-defined transformations and reactions can be observed at various well-defined positions on the surface and even internally. The integration of magnetic copper centers into cavities (violet tetrahedra) of exactly the right size is described.

Angew. Chem. **2001**, *113*, 4158–4161

A. Müller,* E. Krickemeyer, H. Bögge, M. Schmidtmann, P. Kögerler, C. Rosu, E. Beckmann 4034–4037

"Nanoobjects" by Self-Assembly Concomitant with Modifications under Alterable Boundary Conditions: Incorporation of Paramagnetic Metal Centers (Cu^{2+}) in Ring-Shaped Molybdenum-Oxide Based Clusters

Keywords: cluster compounds · magnetic properties · nanostructures · polyoxometalates · self-assembly

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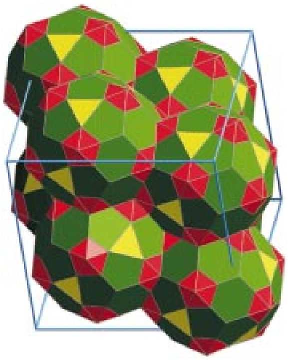
The closest cubic approximant to the $MCd_{5.7}$ (M = Ca, Yb) quasicrystals known so far, namely $Ca_{13}Cd_{76}$, was obtained by high-temperature reaction of the elements. It exhibits a new type of structure for intermetallic compounds with an unprecedented arrangement of triacontahedral clusters (see structure), which could prove useful in modeling the structures of the $MCd_{5.7}$ quasicrystals.



Angew. Chem. **2001**, *113*, 4161–4163

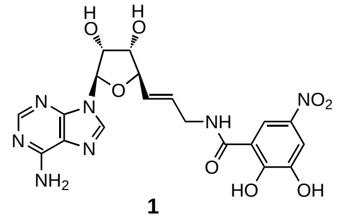
C. P. Gómez,* S. Lidin 4037–4039

Structure of $Ca_{13}Cd_{76}$: A Novel Approximant to the $MCd_{5.7}$ Quasicrystals (M = Ca, Yb)

Keywords: cadmium · calcium · high-temperature chemistry · quasicrystals · solid-state structures

---

With an IC_{50} value of 9 nM, 1 is the most potent known disubstrate inhibitor for catechol-*O*-methyltransferase (COMT). Inhibition of COMT is of significant interest in the therapy of Parkinson's disease since it ensures that a larger percentage of orally administered L-dopa reaches—in the form of dopamine—its target in the brain. The X-ray crystal structure of a complex formed by COMT and **1** has been solved at 2.6-Å resolution.



1

Angew. Chem. **2001**, *113*, 4164–4166

C. Lerner, A. Ruf, V. Gramlich, B. Masjost, G. Zürcher, R. Jakob-Roetne, E. Borroni, F. Diederich* ... 4040–4042

X-ray Crystal Structure of a Bisubstrate Inhibitor Bound to the Enzyme Catechol-*O*-methyltransferase: A Dramatic Effect of Inhibitor Preorganization on Binding Affinity

Keywords: drug research · enzyme inhibitors · medicinal chemistry · structure–activity relationships · transferases

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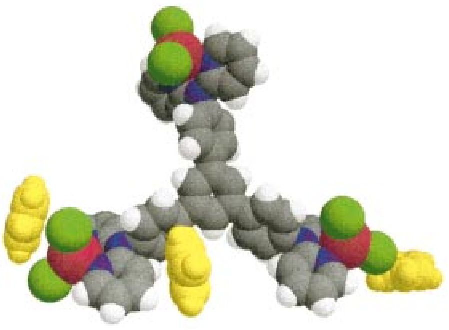
Binding benzene: A novel blue luminescent star-shaped Zn^{II} complex has been found to be able to detect benzene selectively by fluorescent quenching. This is attributed to the compound's high affinity to benzene, as demonstrated in the crystal structure (see picture; yellow: benzene, red: zinc).



Angew. Chem. **2001**, *113*, 4166–4169

J. Pang, E. J.-P. Marcotte, C. Seward, R. S. Brown,* S. Wang* 4042–4045

A Blue Luminescent Star-Shaped Zn^{II} Complex that Can Detect Benzene

Keywords: benzene · luminescence · N ligands · sensors · stacking interactions · zinc

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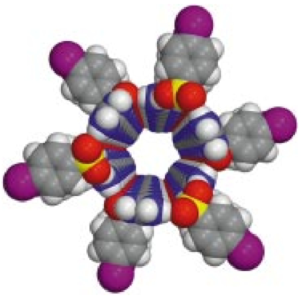
Inclusion compounds based on a flexible hydrogen-bonded sheet of guanidinium ions and sulfonate moieties display lamellar and tubular architectures, depending on the guest and the organic substituent attached to the sulfonate. The observed single-crystal architectures resemble lamellar and hexagonal microstructures (see picture) in block copolymers and surfactant assemblies.



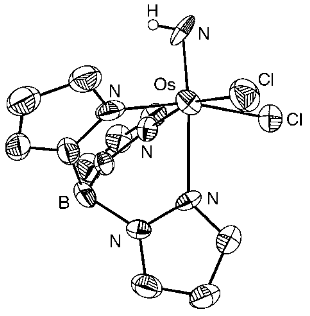
Angew. Chem. **2001**, *113*, 4169–4172

M. J. Horner, K. T. Holman, M. D. Ward* 4045–4048

Lamellae-Nanotube Isomerism in Hydrogen-Bonded Host Frameworks

Keywords: clathrates · crystal engineering · inclusion compounds · nanotubes · self-assembly · template synthesis

Trapped by a proton: In the formation of $Os^{II}–N_2–Os^{II}$ dimers, an $Os^{V}\equiv N$ complex has been invoked as a transient intermediate but not isolated. Herein conditions are reported that allow $Os^{V}\equiv N$ species to be trapped either in acidic, aqueous solutions as a neutral osmium(v) imido complex ($Os^{V}NH$, see structure) or in non-aqueous solvents, with high concentrations of added reductant, by N^- ion transfer before coupling can occur.



Angew. Chem. **2001**, *113*, 4173–4175

M. H. V. Huynh,* P. S. White, K. D. John, T. J. Meyer* 4049–4051

Isolation and Characterization of the Osmium(v) – Imido Complex $[Os^{V}(Tp)(Cl)_2(NH)]$

Keywords: electrochemistry · N ligands · osmium · protonation · tripodal ligands

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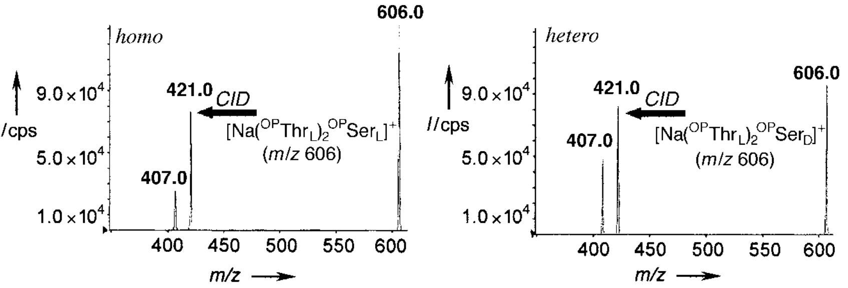
Identification and quantification of the enantiomeric excess of *O*-phosphoserine (^{OP}Ser) residues from post-translational modified proteins is now possible by the application of a very reproducible and sensitive mass spectrometric method. This technique is based on the different mass-spectral fragmentation patterns of the diastereomeric cluster ions generated in water/methanol solutions of the analyte ($^{OP}Ser_{D/L}$) with a suitable chiral compound ($^{OP}Thr_L$) by collision-induced dissociation (CID; see mass spectra).



Angew. Chem. **2001**, *113*, 4175–4178

G. Fago, A. Filippi, A. Giardini, A. Laganà, A. Paladini, M. Speranza* 4051–4054

Chiral Recognition of *O*-Phosphoserine by Mass Spectrometry

Keywords: chirality · enantioselectivity · mass spectrometry · proteomics

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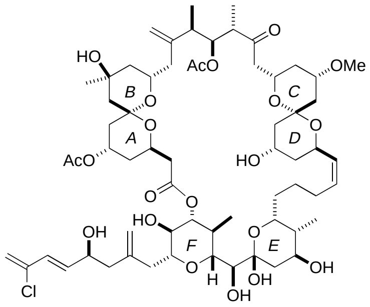
As an exceptionally potent antimitotic macrolide, altohyrtin A/spongistatin **1** shows great promise in cancer chemotherapy but its extreme scarcity in the natural sponges has halted its further preclinical development. A highly stereocontrolled total synthesis, which exploits boron-mediated aldol bond constructions, has been realized to provide, for the first time, a useful amount of synthetic material.



1

Angew. Chem. **2001**, *113*, 4179–4184

I. Paterson,* D. Y.-K. Chen, M. J. Coster, J. L. Aceña, J. Bach, K. R. Gibson, L. E. Keown, R. M. Oballa, T. Trieselmann, D. J. Wallace, A. P. Hodgson, R. D. Norcross 4055–4060

Stereocontrolled Total Synthesis of (+)-Altohyrtin A/Spongistatin 1

Keywords: aldol reactions · macrolides · natural products · total synthesis

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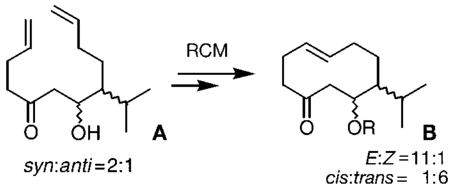
Even 10-membered rings can be obtained by ring-closing metathesis (RCM). The synthesis of carbocycle **B** by RCM, which is the key step in the synthesis of the pine-resin sesquiterpene 1,6-germacradien-5-ol, was improved by protecting the hydroxy group of the precursor bisolefin **A** as a bulky *tert*-butyldimethylsilyl ether and by complexing its carbonyl group with $Ti(OiPr)_4$.



Angew. Chem. **2001**, *113*, 4184–4186

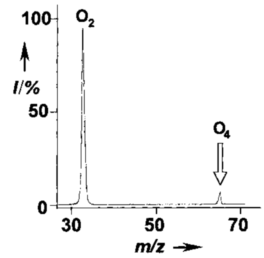
M. Nevalainen, A. M. P. Koskinen* 4060–4062

Synthesis of a 10-Membered Carbocycle By Olefin Metathesis

Keywords: carbocycles · cyclization · metathesis · ruthenium · terpenoids

Although suggested by Lewis in 1924 and theoretically predicted, O_4 has so far proved extremely elusive, defying all attempts at the positive experimental detection of a bound, intact O_4 species. The search has now been brought to an end by the conclusive proof, achieved by neutralization–reionization mass spectrometry (see picture), of the existence of intact O_4 as a gas-phase species with a lifetime in excess of 1 µs, whose dissociation requires overcoming a barrier of the order of 10 kcal mol^{-1}.

Angew. Chem. **2001**, *113*, 4186–4189



F. Cacace,* G. de Petris,
A. Troiani 4062–4065

Experimental Detection of Tetraoxygen

Keywords: ion–molecule reactions · mass spectrometry · metastable compounds · oxygen

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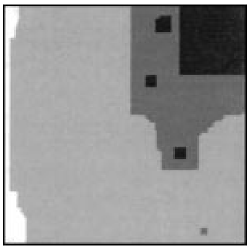
An accurate model of the surface growth of one of the most important industrial zeolites, zeolite A, has been created. Comparison of the simulation (see picture) with experimental data in the form of atomic force micrographs highlights the non-diffusion-limited nature of zeolite growth and provides the first ever quantification of fundamental crystal growth processes in zeolites.

Angew. Chem. **2001**, *113*, 4189–4191



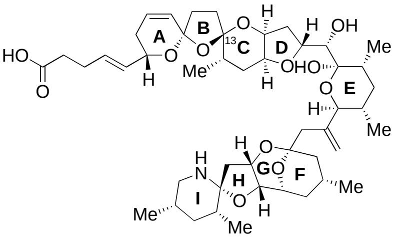
J. R. Agger,* N. Hanif,
M. W. Anderson* 4065–4067

Fundamental Zeolite Crystal Growth Rates from Simulation of Atomic Force Micrographs

Keywords: computer chemistry · crystal growth · scanning probe microscopy · surface chemistry · zeolites

---

Previously attempted spirocyclizations to form the ABCD ring system of azaspiracid (**1**) have proven unsuccessful owing to the anomeric effects that favor the formation of the undesired 13*S* diastereomer. By the use of a hydrogen bond donor as an auxiliary group, such anomeric effects were successfully overcome. Thus, the first synthesis of the ABCD ring system of azaspiracid with the proper 13*R* configuration of the C13 stereocenter was achieved.



1

Angew. Chem. **2001**, *113*, 4192–4195

K. C. Nicolaou,* W. Qian, F. Bernal,
N. Uesaka, P. M. Pihko,
J. Hinrichs 4068–4071

Synthesis of the ABCD Ring System of Azaspiracid

Keywords: azaspiracid · natural products · spiro compounds · stereoelectronic effects

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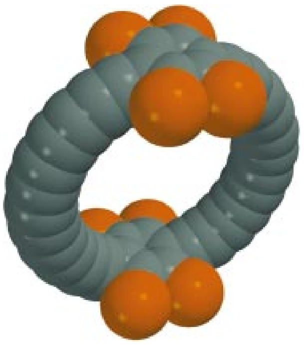
The smallest [*n.n*]cyclophyne known, [12.12]paracyclophanedodecaynes $C_{36}H_8$ and $C_{36}Cl_8$ (see picture), were generated by [2+2] cycloreversion of its precursor under photolytic and mass spectrometric conditions. The stepwise loss of chlorine atoms from the anion of the octachloro derivative $C_{36}Cl_8^-$ produced a carbon cluster anion C_{36}^- in the gas phase.

Angew. Chem. **2001**, *113*, 4196–4198

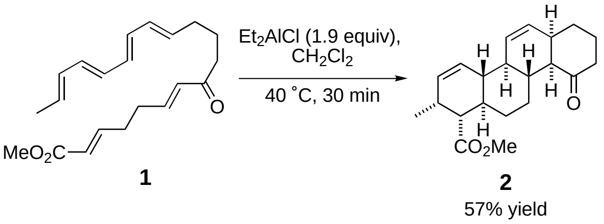


Y. Tobe,* R. Furukawa, M. Sonoda,
T. Wakabayashi 4072–4074

[12.12]Paracyclophanedodecaynes $C_{36}H_8$ and $C_{36}Cl_8$: The Smallest Paracyclophynes and Their Transformation into the Carbon Cluster Ion C_{36}^-

Keywords: carbon clusters · cyclophanes · fullerenes · macrocycles · polyynes

Four C–C bonds, four rings, and eight contiguous stereocenters in one go! Tetracyclic product **2**, which results on warming simple acyclic precursor **1** with a mild Lewis acid, is formed through an efficient and highly stereoselective domino sequence of two intramolecular Diels–Alder reactions. Pharmacologically important norsteroids are just one potential application of this extremely effective approach to fused polycyclic systems.



Angew. Chem. **2001**, *113*, 4198–4200

M. Nörret, M. S. Sherburn* 4074–4076

The Zipper-Mode Domino Intramolecular Diels–Alder Reaction: A New 0→ABCD Strategy for Steroids and Related Compounds

Keywords: cycloaddition · diastereoselectivity · domino reactions · polycycles · steroids

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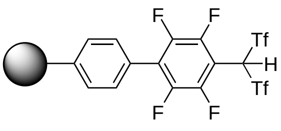
Several advantages over inorganic solid acids such as zeolites and perfluororesinsulfonic acids such as Nafion are offered by the new reusable polystyrene-bound catalyst **1**: a broader range of applications, improved yields, improved selectivity, and milder reaction conditions. Tf = F_3CSO_2.



1

Angew. Chem. **2001**, *113*, 4201–4203

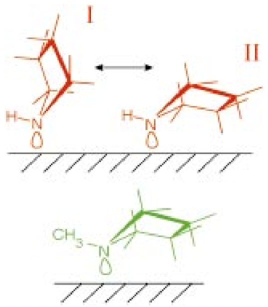
K. Ishihara, A. Hasegawa, H. Yamamoto* 4077–4079

Polystyrene-Bound Tetrafluorophenylbis(triflyl)methane as an Organic-Solvent-Swellable and Strong Brønsted Acid Catalyst

Keywords: Brønsted acids · fluorine · heterogeneous catalysis · superacidic systems · supported catalysts

---

Negative differential resistance (NDR), mediated by vibrational excitation, is strongly dependent on molecular structure and dynamics, according to scanning tunneling microscopy on Cu(001)-bound pyrrolidine and *N*-methylpyrrolidine at 9 K. Tunneling electrons cause the former to switch between conformations I and II (see picture), so that NDR is observed. The methyl group of of the latter compound restricts it to a single conformation (see picture), and a linear current–voltage characteristic results.



Angew. Chem. **2001**, *113*, 4204–4206

J. Gaudioso, W. Ho* 4080–4082

Steric Turnoff of Vibrationally Mediated Negative Differential Resistance in a Single Molecule

Keywords: molecular devices · molecular dynamics · nitrogen heterocycles · scanning probe microscopy · vibrational spectroscopy

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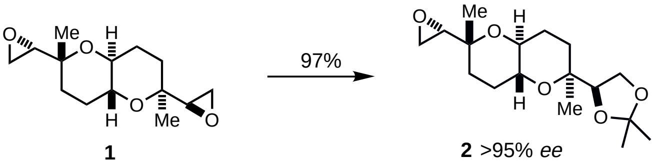
Exploitation of molecular symmetry can greatly improve the efficiency of syntheses. The symmetry embedded in the centrosymmetric AB dioxepane fragment of hemibrevetoxin B was exploited for the first time in the preparation of an established intermediate in its total synthesis. Desymmetrization of the centrosymmetric diepoxide **1** by enantioselective epoxide hydrolysis followed by acetonization gave the known synthetic intermediate **2**.



Angew. Chem. **2001**, *113*, 4206–4208

J. M. Holland, M. Lewis, A. Nelson* 4082–4084

First Desymmetrization of a Centrosymmetric Molecule in Natural Product Synthesis: Preparation of a Key Fragment in the Synthesis of Hemibrevetoxin B

Keywords: asymmetric synthesis · desymmetrization · heterocycles · natural products

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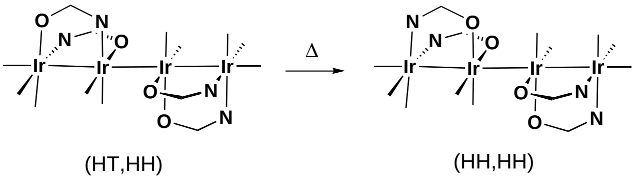
Binuclear complexes with head-to-tail (HT) configurations are appropriate for building tetrametallic chains, contrary to previous speculations. Moreover, the isolated HT,HH tetrametallic species are converted into the thermodynamically more stable HH,HH compounds (see scheme).



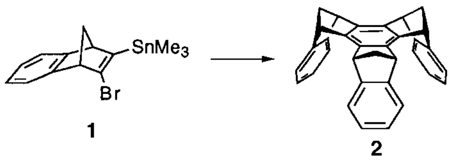
Angew. Chem. **2001**, *113*, 4208 – 4210

C. Tejel, M. A. Ciriano,* B. E. Villarroya, R. Gelpi, J. A. López, F. J. Lahoz, L. A. Oro* .... 4084 – 4086

Discrete Mixed-Valence Metal Chains: Iridium Pyridonate Blues

Keywords: iridium • metal – metal interactions • N,O ligands

The challenge to generate *all-syn* architecture has prompted the synthesis of *syn* cyclotrimers **2** from racemic bromotrimethylstannyl polycyclic alkenes **1**. The *syn*-selective Cu^I-catalyzed cyclotrimerization process is both regio- and chemoselective.



Angew. Chem. **2001**, *113*, 4210 – 4213

S. Cossu,* C. Cimenti, P. Peluso, A. Paulon, O. De Lucchi .... 4086 – 4089

Enantiomeric Discrimination in a Reiterative Domino Coupling Process: Cu^I-mediated *Syn* Cyclotrimerization of Racemic Polycyclic Trimethylstannyl Bromonorbornadienes

Keywords: C–C coupling • chemoselectivity • molecular recognition • polycycles • regioselectivity

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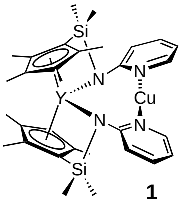
The use of a Me$_2$Si-bridged amido-cyclopentadienyl ligand containing pendant pyridine functionality allows clean "yttrate metathesis" to occur and the synthesis of the unusual C_2-symmetric Y/Cu bimetallic compound **1**.



Angew. Chem. **2001**, *113*, 4213 – 4216

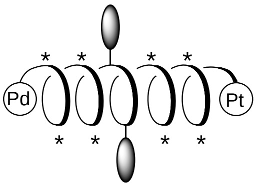
M. S. Hill,* P. B. Hitchcock .. 4089 – 4092

Yttrate Metathesis: Ligand Design for the Controlled Synthesis of f-Block Heterobimetallic Compounds

Keywords: copper • cyclopentadienyl ligands • metathesis • N ligands • yttrium

---

Exciton-coupled circular dichroism of the porphyrin Soret band of triblock copolymers prepared from chiral isocyanide monomers and an achiral tetraphenylporphyrin derivative (TPP) provides a novel method for determining the helical sense of poly(aryl isocyanide)s (see the schematic representation of the structure).



Angew. Chem. **2001**, *113*, 4216 – 4218

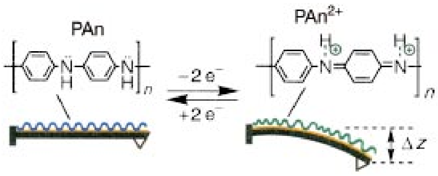
F. Takei, H. Hayashi, K. Onitsuka, N. Kobayashi, S. Takahashi* 4092 – 4094

Helical Chiral Polyisocyanides Possessing Porphyrin Pendants: Determination of Helicity by Exciton-Coupled Circular Dichroism

Keywords: circular dichroism • helical structures • polyisocyanides • polymers • porphyrinoids

---

Bent by oxidation! A polyaniline (PAn, blue) coated cantilever acts as an electro-driven microdevice. Reversible oxidation/reduction of the PAn results in reversible deflection of the cantilever (see picture) originating from the electrostatic repulsion of the charged polymer chains of PAn^{2+} (green).



Angew. Chem. **2001**, *113*, 4219 – 4221

M. Lahav, C. Durkan, R. Gabai, E. Katz, I. Willner,* M. E. Welland .. 4095 – 4097

Redox Activation of a Polyaniline-Coated Cantilever: An Electro-Driven Microdevice

Keywords: electrochemistry • interfaces • molecular devices • polymers • thin films

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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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