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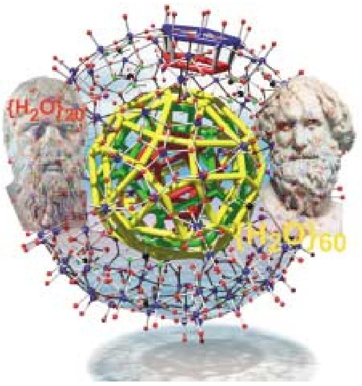
2002
41/19
Pages 3509–3722

COVER PICTURE

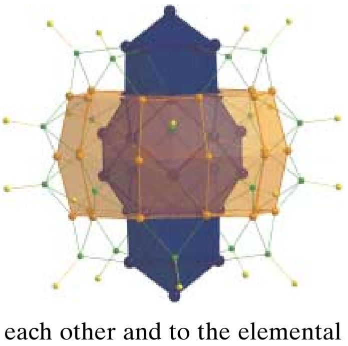
The cover picture shows a novel hierarchic endohedral clusterization of H_2O molecules in the form of a dodecahedron ($(H_2O)_{20}$, red), a further "mounted" dodecahedron (green), and a rhombicosidodecahedron ($(H_2O)_{60}$, yellow). The shell/host (Mo atoms blue, O red) is built up by 12 pentagonal $\{(Mo)Mo_5\}$ type building blocks (one is highlighted as a blue ring),which are connected by 30 Mo^V_2 linkers with the consequence that 20 nanosized Mo_9O_9 pores/rings of classical crown ether quality are formed in which 20 guanidinium cations are encapsulated (C black, N green). The Mo^V_2 type linkers are stabilized by $PO_2H_2^-/SO_4^{2-}$ ligands (P/S purple). As the clusterization in the cavity takes place after filling the receptors/pores at the cluster surface with guests, a process is modeled by which a cell converts an extracellular molecular signal into a response. The representative red ring below the blue ring is marked out by the 60 H_2O ligands coordinated to the pentagonal Mo units, which altogether form a rhombicosidodecahedron (not shown completely). As the geometric forms described are those of Platonic and Archimedean solids Plato and Archimedes feel involved. Further details are reported by A. Müller et al. on p. 3756 ff.



REVIEWS

Contents

How metallic are gallium and aluminum clusters? To answer this question detailed information about the structures and physical properties of as many metalloid cluster compounds as possible must be collected—not an easy task as the synthesis of these compounds is anything but easy. Like elemental gallium the clusters of gallium form a variety of different structures, these in fact bear a complicated resemblance to each other and to the elemental forms. By way of introduction the picture shows the $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$ cluster, one of the largest metalloid clusters structurally characterized to date.



Angew. Chem. **2002**, *114*, 3683–3704

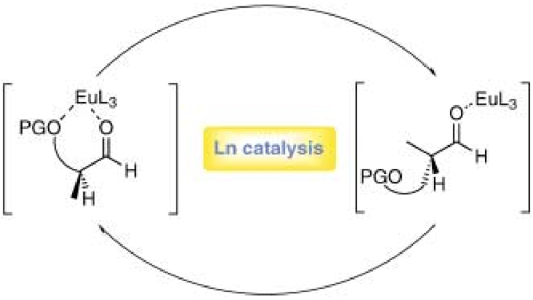
A. Schnepf, H. Schnöckel* .. 3533–3554

Metalloid Aluminum and Gallium Clusters: Element Modifications on the Molecular Scale?

Keywords: aluminum · cluster compounds · gallium · metal–metal interactions · structure elucidation

1433-7851/02/4119-3511 $ 20.00+.50/0

High coordination numbers and fast ligand association and dissociation: Lanthanide complexes are ideal candidates for use as homogeneous catalysts in many organic reactions, for example, the aldol addition, which can either occur via a chelate or a nonchelate intermediate (see scheme; PG = protecting group).



Angew. Chem. **2002**, *114*, 3705 – 3722

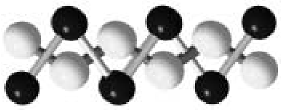
K. Mikami,* M. Terada, H. Matsuzawa .... 3555 – 3572

"Asymmetric" Catalysis by Lanthanide Complexes

Keywords: asymmetric catalysis · enantioselectivity · coordination chemistry · lanthanides · Lewis acids

MINIREVIEW

Gold is more "relativistic" than any other element before fermium. One consequence is the large electronegativity of Au, which qualitatively explains the stability of (solid or liquid) cesium auride, Cs^+Au^- (see picture), and other systems with Au^- ions. The structure and bonding of the recently discovered $CsAu \cdot NH_3$ is discussed. Other ammoniates and some future possibilities are outlined.



Angew. Chem. **2002**, *114*, 3723 – 3728

P. Pyykkö* .... 3573 – 3578

Relativity, Gold, Closed-Shell Interactions, and $CsAu \cdot NH_3$

Keywords: cesium · closed-shell interactions · computer chemistry · gold · relativistic effects

VIPs

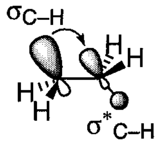
The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.org

Syntheses and Crystal Structures of the New Ag-S Clusters $[Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4(triphos)_4]$ and $[Ag_{188}S_{94}(PR_3)_{30}]$	X.-J. Wang, T. Langetepe, C. Persau, B.-S. Kang, G. M. Sheldrick, D. Fenske*	◆
Ethane and Ethylidene Dicarboxylates from the Ruthenium(II)-Catalyzed Disproportionative Addition of Carboxylic Acids to Ethene	T. Funaioli,* F. Marchetti, G. Fachinetti*	◆
Cell-Free Biosynthesis of Fluoroacetate and 4-Fluorothreonine in *Streptomyces cattleya*	C. Schaffrath, S. L. Cobb, D. O'Hagan*	◆
Selective Measurements of a Nitroxide – Nitroxide Distance of 5 nm and a Nitroxide – Copper Distance of 2.5 nm in a Terpyridine-Based Copper(II) Complex by Pulse EPR Spectroscopy	E. Narr, A. Godt, G. Jeschke*	◆
A Synthesis Route to Enantiomerically Pure Jasmonoids	M. Ernst, G. Helmchen*	

1433-7851/02/4119-3512 $ 20.00+.50/0

ESSAY

When will we accept the quantum nature of chemistry? A critical view on how we teach the origin of rotational barriers (see picture) emphasizes the importance of continuously updating what we teach our students.



Angew. Chem. **2002**, *114*, 3729 – 3732

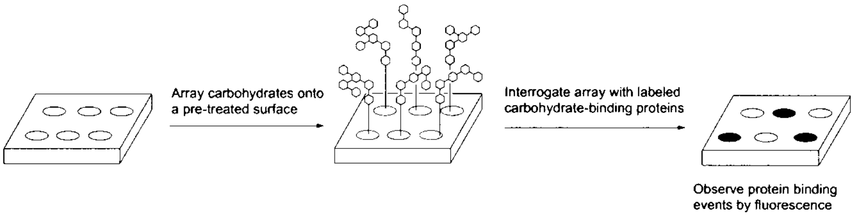
P. R. Schreiner* .... 3579 – 3582

Teaching the Right Reasons: Lessons from the Mistaken Origin of the Rotational Barrier in Ethane

Keywords: alkanes · computations · conformational analysis · hyperconjugation · rotational barriers

HIGHLIGHTS

Rapid identification of carbohydrate-binding events that leads to a better understanding of signaling processes is being achieved through the development of carbohydrate microarrays. In the example shown, array carbohydrates are first immobilized on a pretreated surface and then interrogated with fluorescently labeled carbohydrate-binding proteins; the binding event can then be observed by fluorescence spectroscopy.



Angew. Chem. **2002**, *114*, 3733 – 3736

K. R. Love, P. H. Seeberger* 3583 – 3586

Carbohydrate Arrays as Tools for Glycomics

Keywords: carbohydrates · microarrays · monolayers · oligosaccharides · self-assembly

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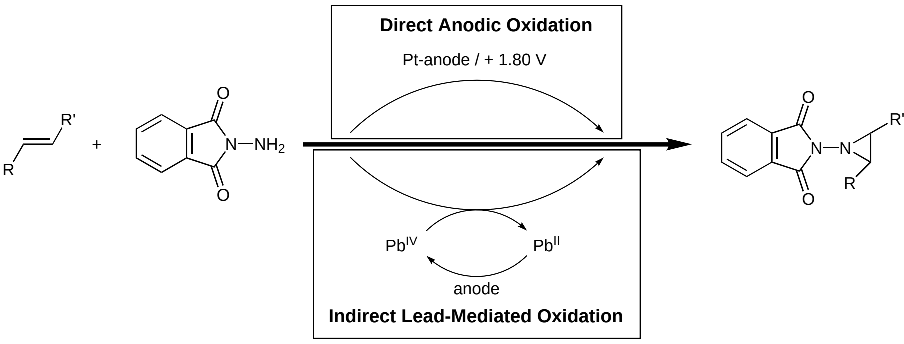
Less lead is good, no lead is better still: Environmentally friendly aziridinations of alkenes can be conducted under either indirect lead-mediated or direct metal-free electrochemical potential-controlled oxidation conditions using suitable hydrazine derivatives. In economic and ecological terms, the method represents another important step in electroorganic synthesis towards future methods that avoid the production of toxic waste.



Angew. Chem. **2002**, *114*, 3737 – 3740

G. Hilt* .... 3586 – 3588

Direct Electrochemical Aziridination of Alkenes under Metal-Free Conditions

Keywords: alkenes · electrochemistry · heterocycles · lead · oxidations

CORRESPONDENCE

Not the definitive work but rather contributions to a body of literature have recently been portrayed in a Highlight in *Angewandte Chemie* according to the author of this Correspondence. Herein, misrepresentations and omissions with regard to the literature on microwave chemistry are addressed.

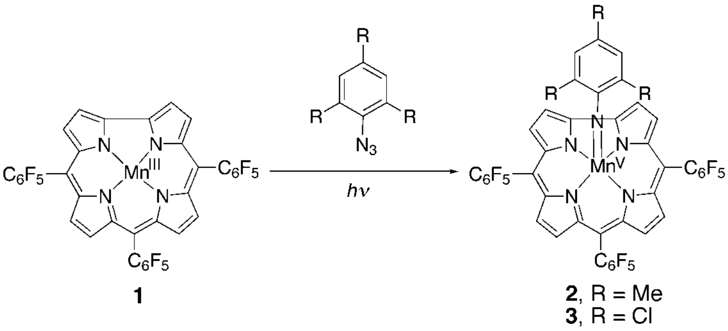
Angew. Chem. **2002**, *114*, 3741 – 3743

C. R. Strauss* .... 3589 – 3591

Microwave-Assisted Reactions in Organic Synthesis—Are There Any Nonthermal Microwave Effects?

Keywords: correspondence · microwave chemistry · synthetic methods

At last, terminal imido complexes of manganese(v), the postulated intermediates in aziridination and amination reactions, have been prepared. The structurally well-defined (imido)manganese(v) corroles, **2** and **3**, are easily synthesized from manganese(III) corroles with organic azides under photolysis conditions and react with electron-rich nucleophiles such as organic phosphanes.



Angew. Chem. **2002**, *114*, 3744–3747

R. A. Eikey, S. I. Khan,
M. M. Abu-Omar* 3592–3595

The Elusive Terminal Imido of Manganese(v)

Keywords: azides · corroles · manganese · multiple bonds · photolysis

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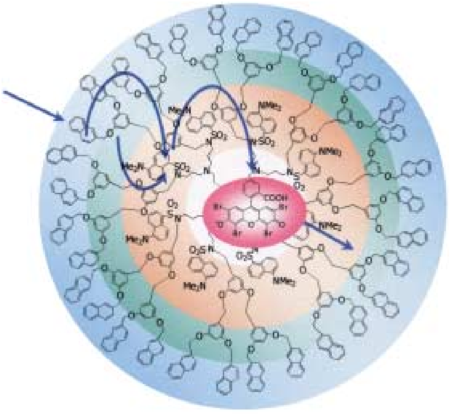
An eosin molecule encapsulated into the dendrimer shown in the picture collects electronic energy from all 64 chromophoric units of the dendrimer, which comprises three different types of chromophore. Efficient intramolecular (within the dendrimer) and intermolecular (dendrimer-host →eosin-guest) energy-transfer processes by a Förster type mechanism, as suggested by the strong overlap between the emission and absorption spectra of the relevant donor and acceptor units.



Angew. Chem. **2002**, *114*, 3747–3750

U. Hahn, M. Gorka, F. Vögtle,*
V. Vicinelli, P. Ceroni, M. Maestri,*
V. Balzani* 3595–3598

Light-Harvesting Dendrimers: Efficient Intra- and Intermolecular Energy-Transfer Processes in a Species Containing 65 Chromophoric Groups of Four Different Types

Keywords: chromophores · dendrimers · energy transfer · eosin · fluorescence

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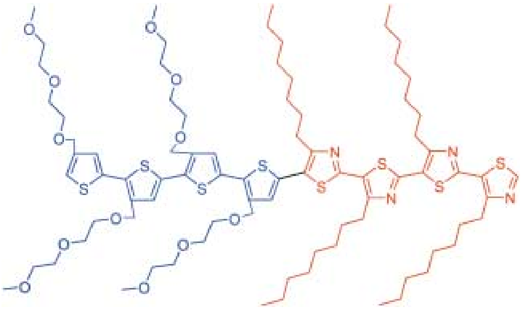
A diodelike rectifying effect was observed in Langmuir–Blodgett monolayers of a p-n junction molecule, the amphiphilic π-conjugated diblock oligomer shown. A reference molecule without the p-n junction feature shows nonrectifying behavior.



Angew. Chem. **2002**, *114*, 3750–3753

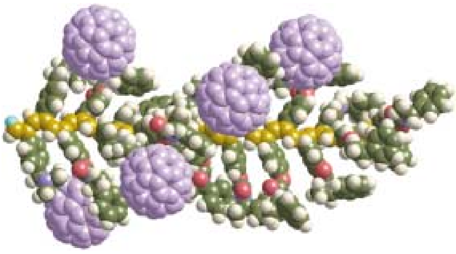
M.-K. Ng, L. Yu* 3598–3601

Synthesis of Amphiphilic Conjugated Diblock Oligomers as Molecular Diodes

Keywords: electronic devices · Langmuir–Blodgett films · polymers · scanning probe microscopy

A question of balls and chains: The copolymerization of an achiral fullerene and an optically active phenylacetylene yields a helical polymer (see picture) where the pendant C_{60} groups adopt a predominant screw-sense along the polymer backbone. The copolymer exhibits an induced circular dichroism in the fullerene chromophoric region.

Angew. Chem. **2002**, *114*, 3754 – 3756



T. Nishimura, K. Takatani, S. Sakurai,
K. Maeda, E. Yashima* ..... 3602 – 3604

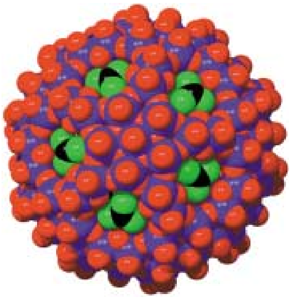
A Helical Array of Pendant Fullerenes on an Optically Active Polyphenylacetylene

Keywords: chirality · circular dichroism · fullerenes · helical structures · polymerization

---

Responsive sensing clusters: By linking {(Mo)Mo$_5$} type building units with different spacers, spherical clusters (nanosponges) having 20 different nanosized and tunable Mo$_n$O$_m$ pores/macrocycles of the type and quality of the classical crown ethers of supramolecular chemistry are formed (see picture of an {Mo$_9$O$_9$}-type host with guanidinium ion $[(NH_2)_3C]^+$ guests; Mo blue, O red, N green, C black). This property allows the development of a novel spherical-surface and nanoporous-cluster chemistry with the possibility of the formation of extended cluster networks (solid-state structures), as well a modeling of cell responses to extracellular signal molecules.

Angew. Chem. **2002**, *114*, 3756 – 3763



A. Müller,* E. Krickemeyer, H. Bögge,
M. Schmidtmann, S. Roy,
A. Berkle .... 3604 – 3609

Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide Based “Nanosponge”: En Route to Sphere-Surface and Nanoporous-Cluster Chemistry

Keywords: host – guest systems · molecular recognition · nanostructures · polyoxometalates · topology

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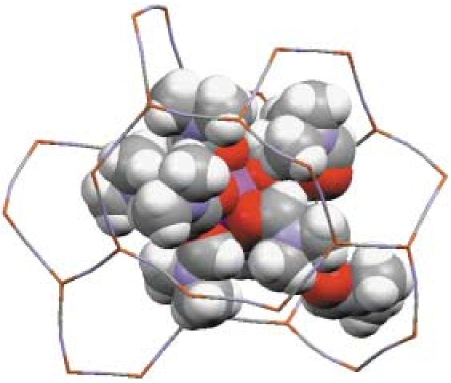
Reaction conditions determine the product: The reaction of GdCl$_3$ and pre-formed K[Cu(CN)$_2$] in DMF leads to a lanthanide – transition-metal complex with a layered structure. Treatment of GdCl$_3$ with discrete quantities of CuCN and KCN, however, yields an inclusion complex with $[Gd(dmf)_8]^{3+}$ ions located within “pockets” (see picture) throughout a three-dimensional array of $[Cu_6(CN)_9]^{3-}$ ions.

Angew. Chem. **2002**, *114*, 3761 – 3763



S. Liu, E. A. Meyers,
S. G. Shore* .... 3609 – 3611

An Inclusion Complex with $[Gd(dmf)_8]^{3+}$ Ions Encapsulated in Pockets of an Anionic Array of $[\{Cu_6(CN)_9\}^{3-}]_\infty$ Units; A Cyanide-Bridged Cu – Gd Layer Structure

Keywords: copper · cyanides · gadolinium · inclusion compounds · layered compounds

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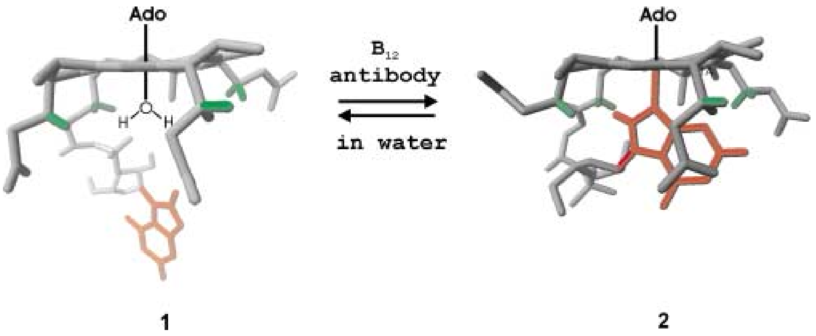
A monoclonal antibody, raised against coenzyme B$_{12}$, binds natural “base-off” analogues **1** of coenzyme B$_{12}$ and restructures them into the “base-on” form **2**.



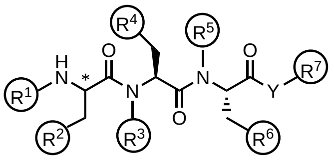
Angew. Chem. **2002**, *114*, 3765 – 3768

R. B. Hannak, R. Konrat, W. Schüler,
B. Kräutler,* M.-T. M. Auditor,
D. Hilvert* .... 3613 – 3616

An Antibody that Reconstitutes the “Base-On” Form of B$_{12}$ Coenzymes

Keywords: antibodies · cofactors · molecular recognition · vitamin B12

Potent mono- and bisubstrate inhibitors of the enzyme protein farnesyltransferase are furnished by a structurally broadly varied compound library derived from the natural product pepticinnamin E (see picture), by a six-to-nine-step solid-phase peptide synthesis. One inhibitor was identified as inducing apoptosis in H-Ras-transformed tumor cells.



Angew. Chem. **2002**, *114*, 3768–3772

M. Thutewohl, L. Kissau, B. Popkirova, I.-M. Karaguni, T. Nowak, M. Bate, J. Kuhlmann, O. Müller, H. Waldmann* 3616–3620

Solid-Phase Synthesis and Biological Evaluation of a Pepticinnamin E Library

Keywords: apoptosis • combinatorial chemistry • farnesyltransferase inhibitors • pepticinnamin E • solid-phase synthesis

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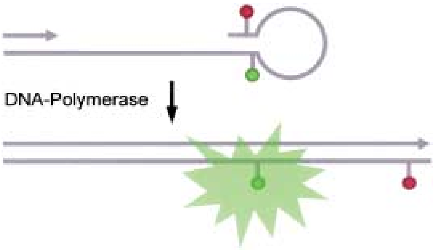
An assay for real-time monitoring of DNA synthesis by DNA polymerases is presented. With the opening of a dual dye-labeled probe, triggered by the progressing enzymatic DNA synthesis, a fluorescent signal is generated (see scheme), enabling the high-throughput quantitative characterization of inhibitors and monitoring of the DNA polymerase reaction in cell lysates.



Angew. Chem. **2002**, *114*, 3778–3780

D. Summerer, A. Marx* 3620–3622

A Molecular Beacon for Quantitative Monitoring of the DNA Polymerase Reaction in Real-Time

Keywords: DNA polymerases • enzyme assay • enzyme inhibitors • high-throughput screening • reporter systems

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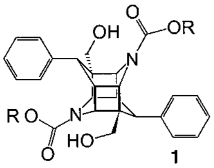
More is not always better: Until now it was considered that modulators of P-glycoprotein-associated multidrug resistance in cancer treatment showed greater inhibitory activity with an increasing number of moieties that could participate in hydrogen bonds. This theory has been questioned for the first time with a new class of symmetrical inhibitors **1** based on hydroxymethyl-3,9-diazatetraasteranes.



1

Angew. Chem. **2002**, *114*, 3772–3775

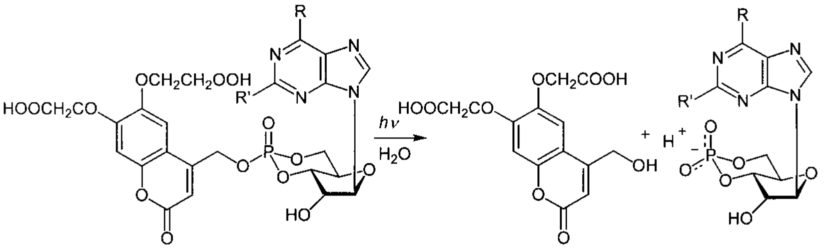
A. Hilgeroth,* J. Molnár, E. De Clercq 3623–3625

Using Molecular Symmetry to Form New Drugs: Hydroxymethyl-Substituted 3,9-Diazatetraasteranes as the First Class of Symmetric MDR Modulators

Keywords: cage compounds • MDR modulators • medicinal chemistry • photochemistry • structure–activity relationships

---

The linear correlation between the increase of fluorescence and the extent of photolysis upon flash photolysis of bis(carboxymethoxy)coumarinylmethyl-caged cAMP (**1**, $R = H$, $R' = NH_2$) and cGMP (**2**, $R = NH_2$, $R' = OH$) allows the visualization and quantification of the release process of the cyclic nucleotides within cells.



1, **2**

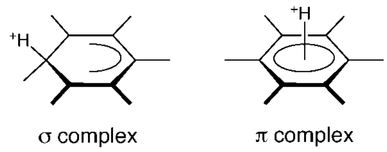
Angew. Chem. **2002**, *114*, 3775–3777

V. Hagen,* S. Frings, J. Bendig, D. Lorenz, B. Wiesner, U. B. Kaupp 3625–3628

Fluorescence Spectroscopic Quantification of the Release of Cyclic Nucleotides from Photocleavable [Bis(carboxymethoxy)coumarin-4-yl]methyl Esters inside Cells

Keywords: fluorescence • ion channels • nucleotides • photolysis • signal transduction

Structure of gas-phase arenium ions: The long-standing controversy about the geometry of protonated benzene is unambiguously solved by IR spectroscopy. The first high-resolution gas-phase spectrum of an arenium ion shows that the σ complex (not the π complex; see picture) is the most stable structure of $C_6H_7^+$.



Angew. Chem. **2002**, *114*, 3781 – 3784

N. Solcà, O. Dopfer* .... 3628 – 3631

Protonated Benzene: IR Spectrum and Structure of $C_6H_7^+$

Keywords: arenium ions · aromatic substitution · carbocations · IR spectroscopy · reactive intermediates

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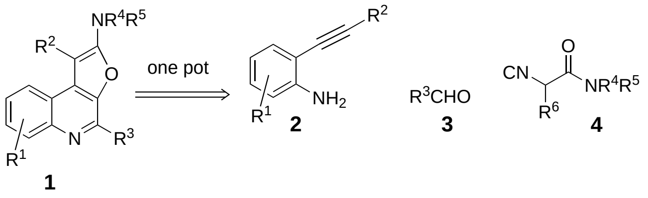
Five bonds form in one pot, from three well-designed yet readily accessible substrates. Simply mixing an *ortho*-alkynyl aniline **2**, an aldehyde **3**, and ammonium chloride in toluene at room temperature, followed by addition of an isocyanoacetamide **4** and heating to reflux, provides the polysubstituted furo[2,3-c]quinoline **1** in good to excellent yield.



Angew. Chem. **2002**, *114*, 3785 – 3787

A. Fayol, J. Zhu* .... 3633 – 3635

Synthesis of Furoquinolines by a Multicomponent Domino Process

Keywords: cycloaddition · multicomponent reactions · nitrogen heterocycles · synthetic methods

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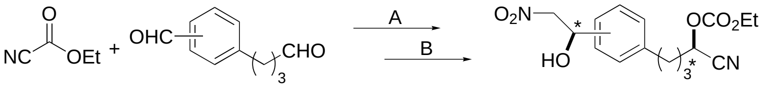
Two catalysts in one! Catalyst tuning with achiral additives effectively constructed and reconstructed a chiral environment around the catalyst [YLi$_3${tris(binaphthoxide)}], which enabled tandem asymmetric catalysis from achiral substrates using a single catalyst component in one pot (see scheme: A = cyanation reaction, B = nitroaldol reaction).



Angew. Chem. **2002**, *114*, 3788 – 3790

J. Tian, N. Yamagiwa, S. Matsunaga, M. Shibasaki* .... 3636 – 3638

An Asymmetric Cyanation Reaction and Sequential Asymmetric Cyanation – Nitroaldol Reaction Using a [YLi$_3${tris(binaphthoxide)}] Single Catalyst Component: Catalyst Tuning with Achiral Additives

Keywords: asymmetric catalysis · asymmetric synthesis · cyanation · multicomponent reactions · yttrium

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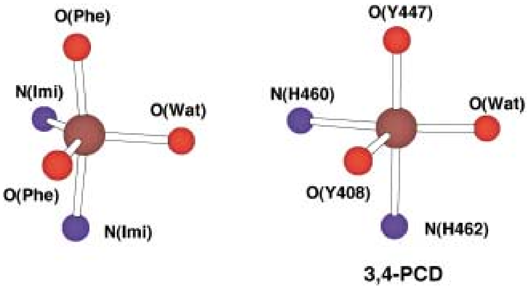
The spectral characteristics as well as the active-site structure of protocatechurate 3,4-dioxygenase (3,4-PCD) have now been mimicked with a ferric aqua complex containing a sterically hindered salen ligand. The coordination sphere of this distorted trigonal-bipyramidal complex (see structures, left; Imi = imino, Phe = phenolate, Wat = water) is the same as that of 3,4-PCD (right; Tyr 408, Tyr 447, His 460, His 462).



Angew. Chem. **2002**, *114*, 3790 – 3793

H. Fujii,* Y. Funahashi ..... 3638 – 3641

A Trigonal-Bipyramidal Ferric Aqua Complex with a Sterically Hindered Salen Ligand as a Model for the Active Site of Protocatechuate 3,4-Dioxygenase

Keywords: bioinorganic chemistry · enzyme models · iron · metalloenzymes · schiff bases

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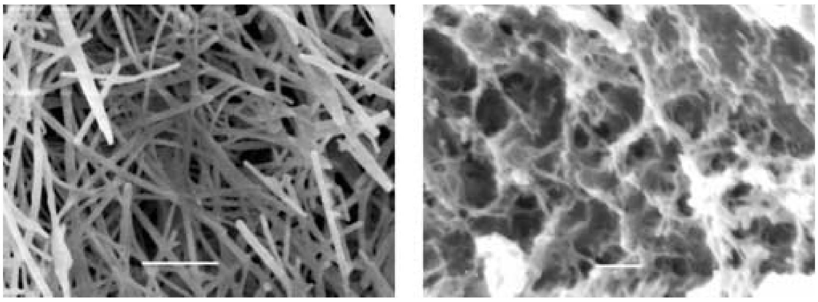
A crystallographic mismatch branching mechanism, rather than molecular self-assembly, controls the architecture of the crystalline structure. Self-organized functional materials with a 3D fibrous network structure (see scanning electron micrographs; right) have been constructed from needlelike crystals of lanosterol:dihydrolanosterol and diisooctylphthalate (left) by using an ethylene/vinyl acetate copolymer as a branching creator.



Angew. Chem. **2002**, *114*, 3793 – 3797

X. Y. Liu,* P. D. Sawant ..... 3641 – 3645

Micro/Nanoengineering of the Self-Organized Three-Dimensional Fibrous Structure of Functional Materials

Keywords: copolymers · crystal growth · nanostructures · networks · soft materials

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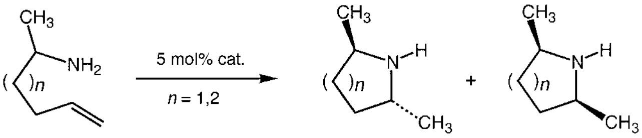
Modification of the metal center in the complexes [Ln{N(TMS)$_2$}$_3$] (Ln = Y, Nd; TMS = trimethylsilyl) is readily achieved by amine elimination in the presence of sterically hindered chelating diamines to provide complexes with substantially augmented catalytic activities and improved stereoselectivities in intramolecular alkene hydroamination (see scheme).



Angew. Chem. **2002**, *114*, 3797 – 3799

Y. K. Kim, T. Livinghouse* . 3645 – 3647

Exceptional Rate Enhancements and Improved Diastereoselectivities through Chelating Diamide Coordination in Intramolecular Alkene Hydroaminations Catalyzed by Yttrium and Neodymium Amido Complexes

Keywords: amino alkenes · cyclization · hydroamination · nitrogen heterocycles · rare-earth metals

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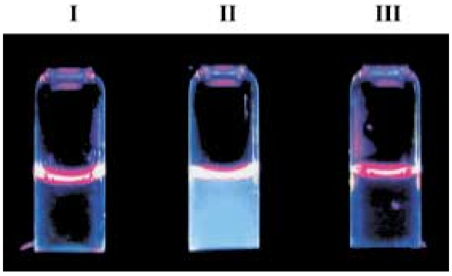
In the living cell is where the authors hope to elucidate the structure of RNA by using their bispyrene-conjugated 2′-O-methyloligoribonucleotide (OMUpy2-I) fluorescence probe, to detect the hybridization with complementary RNA. The picture shows irradiated I) single-stranded OMUpy2-I, II) hybrid of OMUpy2-I with oligoRNA, and III) OMUpy2-I and oligoDNA.



Angew. Chem. **2002**, *114*, 3800 – 3802

A. Mahara, R. Iwase, T. Sakamoto, K. Yamana, T. Yamaoka, A. Murakami* .... 3648 – 3650

Bispyrene-Conjugated 2′-O-Methyloligonucleotide as a Highly Specific RNA-Recognition Probe

Keywords: antisense agents · fluorescent probes · FRET · RNA recognition

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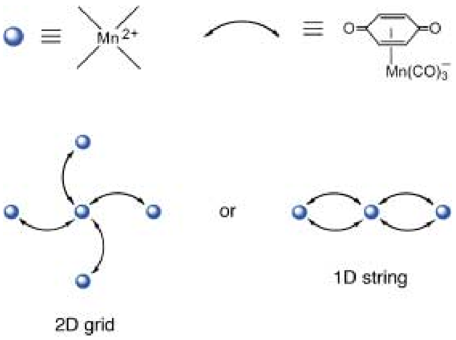
The concentration of metal ions influences the structural characteristics of self-assembled coordination polymers constructed from Mn^{2+} ions and [(η^4-benzoquinone)Mn(CO)$_3$]$^-$ ions. At very low metal-ion concentrations, 1D "string" formations are obtained (see picture), while at higher concentrations, 2D "grid" networks are formed.



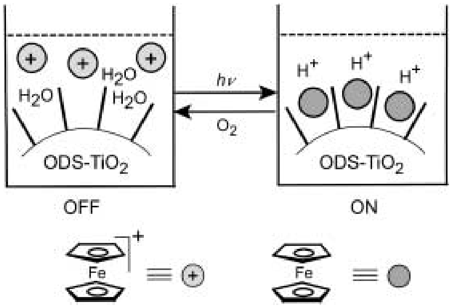
Angew. Chem. **2002**, *114*, 3802 – 3805

M. Oh, G. B. Carpenter, D. A. Sweigart* .... 3650 – 3653

Self-Assembly Using Organometalloligands as Spacers in the Controlled Formation of Isomeric 1D and 2D Supramolecular Quinonoid Networks

Keywords: manganese · polymers · quinones · self-assembly · supramolecular chemistry

Reduction by near-UV light and oxidation by atmospheric oxygen drives the self-reversing photoredox system consisting of a solution of ferrocenium tetrafluoroborate containing a suspension of TiO_2 particles coated with octadecyltrichlorosilane (ODS, see scheme). Reduction of the ferrocenium ions decolorizes the blue solution while the white ODS-TiO_2 particles become yellowish beige. Subsequent oxidation in air regenerates the blue solution and white particles.



Angew. Chem. **2002**, *114*, 3805–3808

M. Muraoka, S. L. Gillett,
T. W. Bell* 3653–3656

Reversible Photoinsertion of Ferrocene into a Hydrophobic Semiconductor Surface: A Chemionic Switch

Keywords: metallocenes · photochemistry · redox chemistry · semiconductors · surface chemistry

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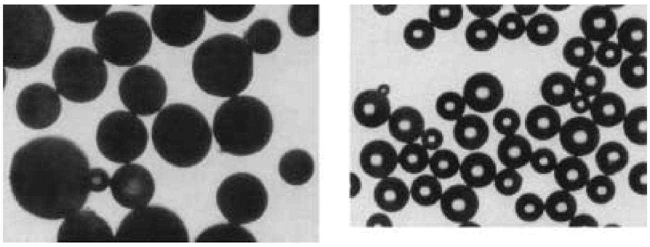
Both macroporous and gel-type high-quality spherical particulate styrene–divinylbenzene resins (see representative optical micrograph) can be synthesized in good yield on a small scale by using an oscillatory baffled reactor. The methodology is tolerant to the use of functional co-monomers.



Angew. Chem. **2002**, *114*, 3808–3811

D. C. Sherrington,* A. Lanver,
H.-G. Schmalz, B. Wilson, X.-W. Ni,
S. Yuan 3656–3659

Gram-Scale Synthesis of Suspension-Polymerized Styrene–Divinylbenzene-Based Resins Using an Oscillatory Baffled Reactor

Keywords: cross-linking · polymerization · styrene · synthetic methods

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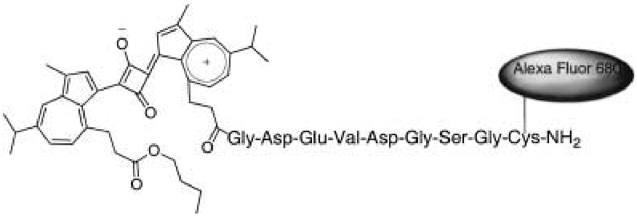
Turning off the light. A fluorescence quencher based on azulene was synthesized which absorbs light in the range of 650 to 800 nm. Since protease sensing was possible with the derivative shown (Alexa Fluor 680 is the fluorochrome), applications in vivo for imaging molecular targets can be expected.



Angew. Chem. **2002**, *114*, 3811–3814

W. Pham, R. Weissleder,
C.-H. Tung* 3659–3662

An Azulene Dimer as a Near-Infrared Quencher

Keywords: azulenes · fluorescence · molecular imaging · proteases · sensors

---

A pair of seven-membered chelate rings are found in the palladium(IV) complex assembled in only a single step from commercially available $[Pd_2(dba)_3]$, tetrachloro-1,2-benzoquinone, and norbornene. The structure consists of a C_2-symmetrical palladaspirocycle framework and an ether ligand, as confirmed by X-ray analysis of the thf complex (see picture).

Angew. Chem. **2002**, *114*, 3814–3817

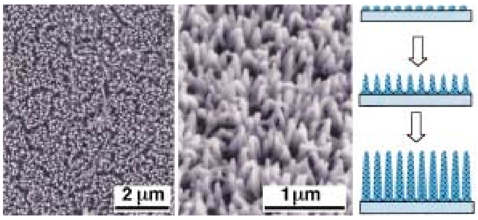
Y. Yamamoto,* T. Ohno,
K. Itoh 3662–3665

Single-Step Assembly of a C_2-Symmetrical Palladium(IV) Spirocyclic Complex

Keywords: Lewis acids · metallacycles · palladium · quinones · structure elucidation

1433-7851/02/4119-3519 $ 20.00+.50/0

Controlling growth: Large arrays of oriented conducting polymer nanowires were prepared by controlled nucleation and growth during a stepwise electrochemical deposition process, without the use of porous membrane supports (see scheme and electron micrographs).



Angew. Chem. **2002**, *114*, 3817–3820

L. Liang, J. Liu,* C. F. Windisch, Jr.,
G. J. Exarhos, Y. Lin 3665–3668

Direct Assembly of Large Arrays of Oriented Conducting Polymer Nanowires

Keywords: aniline · conducting materials · electrochemistry · nanostructures · polymers

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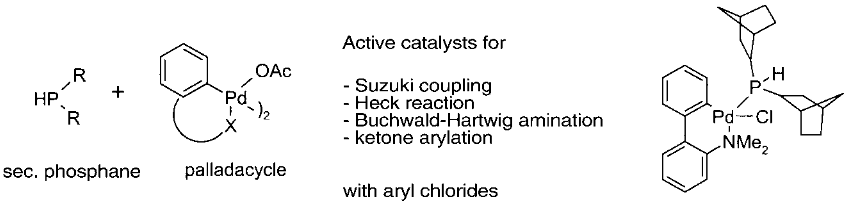
High yields in important Pd-catalyzed reactions of aryl chlorides (see scheme) are obtained with complexes consisting of a palladacycle and a secondary phosphane which could be prepared in situ or isolated. The latter were shown to be stable, and easy to handle in air, and the in situ catalysts allow optimization of the catalyst by variation of the two components.



Angew. Chem. **2002**, *114*, 3820–3823

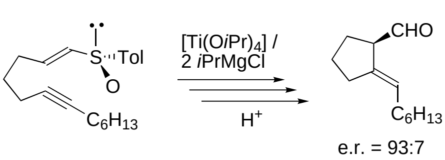
A. Schnyder, A. F. Indolese,* M. Studer,*
H.-U. Blaser 3668–3671

A New Generation of Air Stable, Highly Active Pd Complexes for C–C and C–N Coupling Reactions with Aryl Chlorides

Keywords: aryl chlorides · coupling reactions · homogeneous catalysis · palladacyles · phosphanes

---

Reusing the metal: Combination of the sulfoxide-based asymmetric enyne cyclization (Ti^{II} mediated) and the Pummerer reaction (Ti^{IV} mediated) in tandem was effected by a reagent system consisting of a relay of titanium(II) to titanium(IV), which permits a one-pot synthesis of cyclic aldehydes in an optically active form (see scheme; Tol = *p*-tolyl).



Angew. Chem. **2002**, *114*, 3823–3826

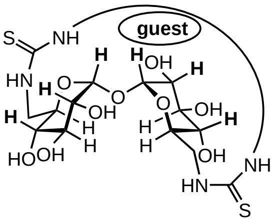
M. Narita, H. Urabe,
F. Sato* 3671–3674

Sulfur-Functionalized Olefins for Titanacycle Formation: Tandem Asymmetric Cyclization and the Pummerer Reaction Based on Sulfoxides Promoted by Titanium(II)-to-Titanium(IV) Relay

Keywords: cyclization · metallacycles · Pummerer reaction · sulfoxides · synthetic methods · titanium

---

The “dark side” of cyclodextrins can be observed in cyclotrehalins, a new family of cyclooligosaccharide receptors made from α,α'-trehalose building blocks. A hydrophobic guest included in these hosts is forced to interact with the β face of the D-glucopyranose subunits (see schematic picture).



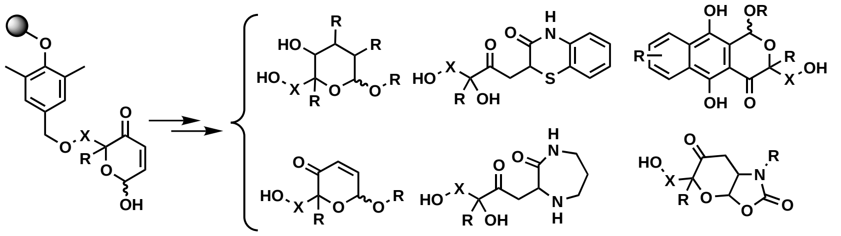
Angew. Chem. **2002**, *114*, 3826–3828

J. M. Benito, J. L. Jiménez Blanco,
C. Ortiz Mellet,*
J. M. García Fernández* 3674–3676

Cyclotrehalins: Cyclooligosaccharide Receptors Featuring a Hydrophobic Cavity

Keywords: carbohydrates · host–guest systems · oligosaccharides · receptors

Antimicrobials, antifungals, anticoccidials, pesticides, and herbicides—druglike scaffolds with potential applications such as these are provided by a combinatorial library containing oxazolediones, naphthoquinones, thiazinones, and diazepinones which were obtained within a few simple steps from solid-supported 2*H*-pyran-3(6*H*)-ones as "polymorphic" key intermediate leads (see scheme).



Angew. Chem. **2002**, *114*, 3829–3832

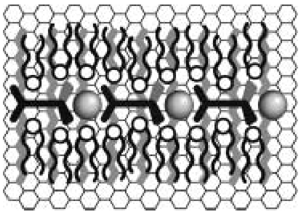
E. A. Couladouros,*
A. T. Strongilos 3677–3680

Generation of Libraries of Pharmacophoric Structures with Increased Complexity and Diversity by Employing Polymorphic Scaffolds

Keywords: combinatorial chemistry · drug design · heterocycles · solid-phase synthesis

---

Multicomponent self-assembly of transition-metal ions, rigid ditopic metal ion receptors, amphiphiles, and alkanes leads to perfectly straight epitaxially oriented nanostructures on the basal plane of graphite (see schematic representation). The long-chain alkanes act as a templating layer that enables the nanoscopic assemblies to be adsorbed in a predictable manner.



Angew. Chem. **2002**, *114*, 3833–3835

D. G. Kurth,* N. Severin,
J. P. Rabe* 3681–3683

Perfectly Straight Nanostructures of Metallosupramolecular Coordination-Polyelectrolyte Amphiphile Complexes on Graphite

Keywords: nanostructures · scanning probe microscopy · self-assembly · single-molecule studies · supramolecular chemistry

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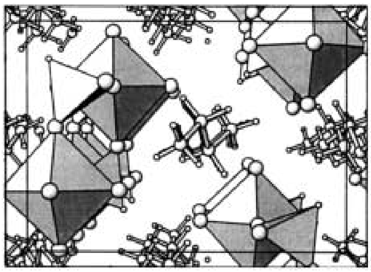
Mild hydrothermal conditions can be used to synthesize the first inorganic–organic hybrid fluorochromium(III) phosphite. The crystal structure (see unit cell) shows that the material consists of double chains of alternating CrO_3F_3 octahedra and HPO_3 tetrahedra. Furthermore, the magnetic behavior indicates the existence of antiferromagnetic interactions.



Angew. Chem. **2002**, *114*, 3835–3837

S. Fernández, J. L. Mesa,* J. L. Pizarro,
L. Lezama, M. I. Arriortua,
T. Rojo* 3683–3685

$(C_2H_{10}N_2)[Cr(HPO_3)F_3]$: The First Organically Templated Fluorochromium(III) Phosphite

Keywords: chromium · magnetic properties · materials science · template synthesis · UV/Vis spectroscopy

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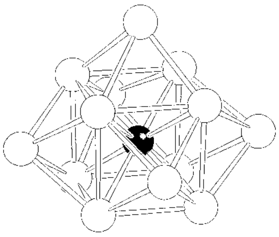
The progressive replacement of Rh with Ni modulates the electronic as well as chemical properties of body-centered $[Rh_{14-x}Ni_x(CO)_9(\mu\text{-}CO)_{16}]^{n-}$ clusters ($x = 0$, $n = 4$; $x = 1$, $n = 5$ (shown here); $x = 2$, $n = 4$; $x = 5$, $n = 2$, 3) and prompts multivalence. The complexes obtained are isostructural, but not isoelectronic.



Angew. Chem. **2002**, *114*, 3837–3840

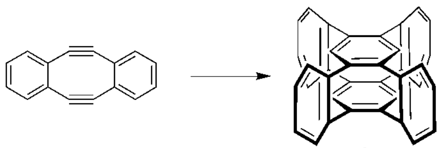
D. Collini, C. Femoni, M. C. Iapalucci,
G. Longoni,* P. H. Svensson,
P. Zanello 3685–3688

Tuning Electronic Behavior of Carbonyl Metal Clusters by Substitution of Interstitial and Capping Atoms

Keywords: carbonyl complexes · cluster compounds · electrochemistry · nickel · rhodium

1433-7851/02/4119-3521 $ 20.00+.50/0

Highly strained but thermally stable: Tetrabenzocyclophane **1**, which was obtained in a four-step synthesis by two Diels–Alder addition reactions (see scheme) sublimes at high temperature, rather than decomposing. The distorted aromatic rings are more reactive with tetracyanoethylene than those in [2.2]paracyclophane. Another consequence of heightened strain is a bathochromic shift of the cyclophane band to 330 nm, the longest wavelength absorption for this band to date.



1

Angew. Chem. **2002**, *114*, 3840–3843

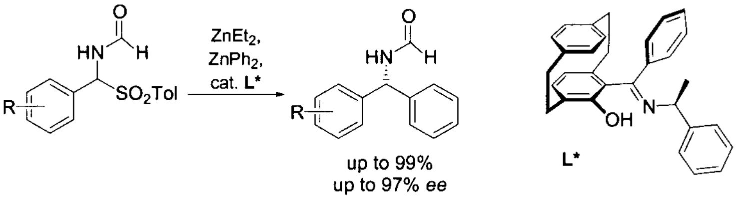
M. Brettreich, M. Bendikov, S. Chaffins, D. F. Perepichka, O. Dautel, H. Duong, R. Helgeson, F. Wudl* 3688–3691

Synthesis, X-ray Structure, and Properties of a Tetrabenzannelated 1,2,4,5-Cyclophane

Keywords: cycloaddition · cyclophanes · density functional calculations · electrochemistry · strained molecules

---

Both planar and central chirality are not necessary in [2.2]paracyclophane-based N,O-ligands to achieve high enantioselectivity: diarylmethylamines are obtained in excellent yields and enantioselectivities up to 97% *ee* in the enantioselective transfer of a phenyl group from organozinc reagents to imines in the presence of catalytic amounts of ketimine **L*** (see scheme).



Angew. Chem. **2002**, *114*, 3844–3846

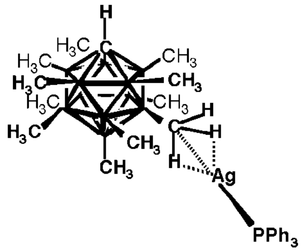
N. Hermanns, S. Dahmen, C. Bolm, S. Bräse* 3692–3694

Asymmetric, Catalytic Phenyl Transfer to Imines: Highly Enantioselective Synthesis of Diarylmethylamines

Keywords: cyclophanes · enantioselectivity · homogeneous catalysis · imines · zinc

---

Both in the solid state and in solution, the complex $[(PPh_3)Ag(HCB_{11}Me_{11})]$ displays significant intermolecular $Ag\cdots H_3C$ interactions. This complex serves as a model for the interaction between a d^{10} metal center and an alkane.



Angew. Chem. **2002**, *114*, 3846–3849

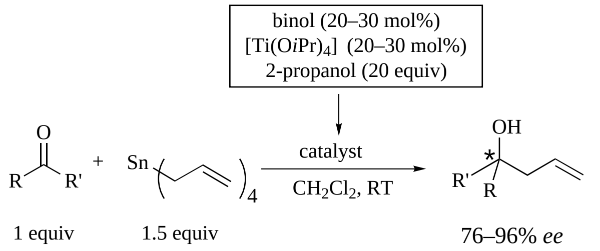
M. J. Ingleson, M. F. Mahon, N. J. Patmore, G. D. Ruggiero, A. S. Weller* 3694–3697

$[(PPh_3)Ag(HCB_{11}Me_{11})]$: A Complex with Intermolecular $Ag\cdots H_3C$ Interactions

Keywords: anions · C–H activation · carboranes · phosphane ligands · silver

---

Allylation of ketones made easy: commercially available reagents can be used at room temperature to transform ketones into homoallylic alcohols with good to excellent enantioselectivities [Eq. (1)]. This process belongs to a rare class of reactions that catalytically form quaternary stereogenic centers.



(1)

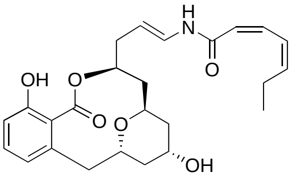
Angew. Chem. **2002**, *114*, 3849–3852

K. M. Waltz, J. Gavenonis, P. J. Walsh* 3697–3699

A Simple, Reliable, Catalytic Asymmetric Allylation of Ketones

Keywords: alcohols · allylation · asymmetric catalysis · titanium

Mimicking nature's biosynthetic pathway to polyketides, a two-step procedure involving allylation followed by ozonolysis was applied five times in total for the construction of the carbon skeleton of apicularen A (**1**). Application of the developed synthetic technology also establishes an entry into designed apicularen analogues.



1: apicularen A

Angew. Chem. **2002**, *114*, 3853 – 3856

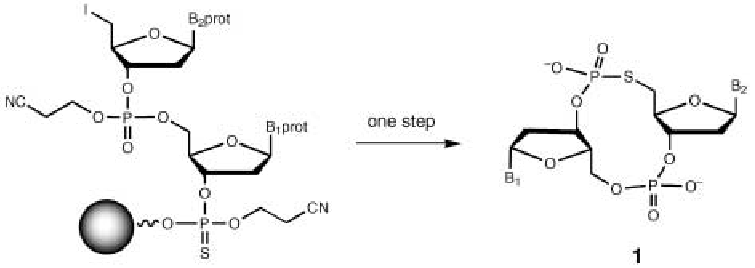
K. C. Nicolaou,* D. W. Kim,
R. Baati .... 3701 – 3704

Stereocontrolled Total Synthesis of Apicularen A and Its $\Delta^{17,18}$ *Z* Isomer

Keywords: biomimetic synthesis · macrolides · natural products · polyketides · total synthesis

---

Only one additional step is required to extend oligonucleotide synthesis to generate cyclic oligonucleotides by standard automated phosphoramidite chemistry. After 5′-iodination, cleavage from the solid support yields phosphorothioate-bridged compounds **1**, which are under investigation as potentially bioactive molecules, in 40 – 80 % yields.



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Angew. Chem. **2002**, *114*, 3856 – 3859

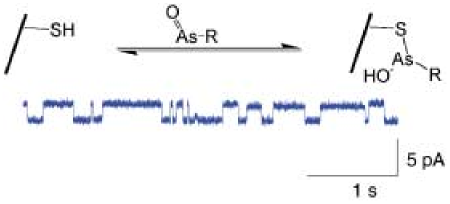
M. Smietana, E. T. Kool* ... 3704 – 3707

Efficient and Simple Solid-Phase Synthesis of Short Cyclic Oligodeoxynucleotides Bearing a Phosphorothioate Linkage

Keywords: cyclization · drug research · oligonucleotides · solid-phase synthesis

---

Arsenic, currents, and pores: Reversible covalent-bond-forming reactions are monitored by single-molecule detection. One reactant, a thiol group, is present on the wall of a protein pore, while the second, an organoarsenic(III) compound is in solution (see scheme). The reaction is detected by observing the current flowing through the pore (see trace), which allows the determination of rate constants with microsecond time resolution.



Angew. Chem. **2002**, *114*, 3859 – 3861

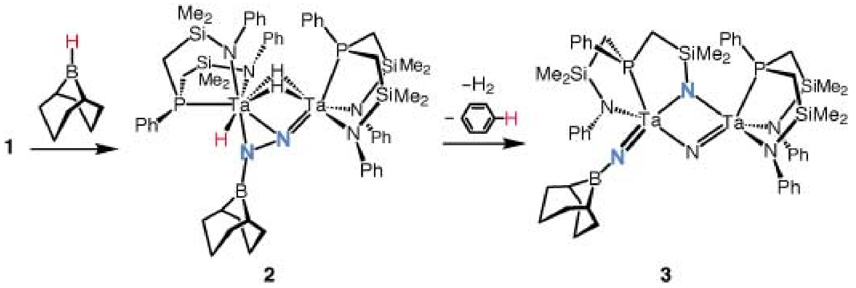
S.-H. Shin, T. Luchian, S. Cheley,
O. Braha, H. Bayley* .... 3707 – 3709

Kinetics of a Reversible Covalent-Bond-Forming Reaction Observed at the Single-Molecule Level

Keywords: analytical methods · arsenic · protein structures · single-molecule studies · sulfur

---

A clean break: Hydroboration of the side-on, end-on N_2 unit of $[\{(NPN)Ta\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)(\mu\text{-}H)_2]$ (**1**; NPN = $PhP(CH_2SiMe_2NPh)_2$) by 9-BBN results in the addition of the B–H bond across the Ta–N_2 moiety to generate a N–B bond and a terminal Ta–H unit (**2**). Surprisingly, this species is unstable in solution. Thus, this hydroboration triggers a cascade of reactions that result in N–N bond cleavage and ancillary ligand rearrangement in the formation of the imide – nitride species **3**.



Angew. Chem. **2002**, *114*, 3861 – 3864

M. D. Fryzuk,* B. A. MacKay,
S. A. Johnson, B. O. Patrick . 3709 – 3712

Hydroboration of Coordinated Dinitrogen: A New Reaction for the N_2 Ligand that Results in Its Functionalization and Cleavage

Keywords: dinitrogen · hydroboration · nitrides · nitrogen fixation · tantalum

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* Author to whom correspondence should be addressed

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