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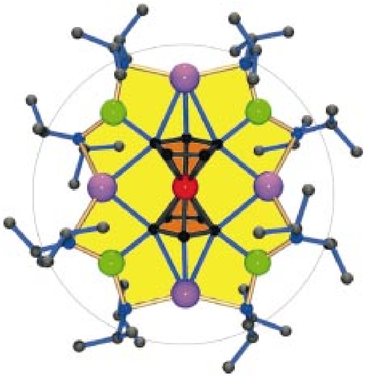
2001
40/20
Pages 3707 – 3926

COVER PICTURE

The cover picture shows the molecular structure of the first ferrocene inverse crown complex. Ferrocene, located in the core, has been fourfold deprotonated at the 1,1′,3,3′-positions by the encapsulating action of the 16-membered tetrasodium–tetramagnesium amide cationic ring which surrounds it. The perimeter of this ring is highlighted in yellow, the sodium and magnesium atoms are shown in violet and green, respectively. More details on the fascinating structure of this inverse crown complex are described by R. Mulvey et al. on pages 3902 ff.

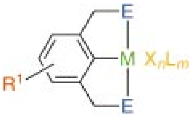


REVIEWS

Asymmetric catalysis is almost synonymous with the use of metals in a chiral environment. Are metals really indispensable for these catalytic processes? Or, can some of their functions be emulated by an organic system? The last few years have witnessed a spectacular advancement in new catalytic methods based on organic molecules. In many cases, extremely high enantioselectivities were achieved with these small organic compounds.

Angew. Chem. **2001**, *113*, 3840 – 3864

Keywords: asymmetric catalysis · chiral auxiliaries · synthetic methods



Pincer ligands are excellent candidates for regulating the reactivity of a metal center through selective ligand substitution (ligand tuning), without affecting the binding mode, particularly in chelation-reinforced metal–carbon bonding (see picture). The implementation of this approach has provided a large variety of platinum group metal complexes that display unprecedented properties. Besides their synthesis, their significance as functional units for the construction of materials is illustrated.

Angew. Chem. **2001**, *113*, 3866–3898

M. Albrecht,
G. van Koten* 3750–3781

Platinum Group Organometallics Based on "Pincer" Complexes: Sensors, Switches, and Catalysts

Keywords: homogeneous catalysis · cyclometalation · materials science · pincer ligands · platinum group metals

ESSAY

The first Nobel Prize in Chemistry was awarded to the Dutch physical chemist Jacobus Henricus van't Hoff in 1901, exactly hundred years ago. His impact on the chemical sciences is unparalleled with concepts ranging from tetrahedra to thermodynamics. He reshaped the discipline of chemistry at a very young age. Through the years, Van't Hoff has inspired many Dutch scientists to perform research on novel stereochemical concepts. The picture shows stereochemical models, which Van't Hoff produced himself.

Angew. Chem. **2001**, *113*, 3899–3905

E. W. Meijer* 3783–3789

Jacobus Henricus van't Hoff; Hundred Years of Impact on Stereochemistry in the Netherlands

Keywords: biography · kinetics · stereochemistry · supramolecular chemistry · thermodynamics

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

Experimental Detection of Tetraoxygen	F. Cacace,* G. de Petris, A. Troiani	◆
[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}^-	Y. Tobe,* R. Furukawa, M. Sonoda, T. Wakabayashi	◆
Side-Wall Functionalization of Carbon Nanotubes	M. Holzinger, O. Vostrowsky, A. Hirsch,* F. Hennrich, M. Kappes, R. Weiss, F. Jellen	◆
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. Timshkin, 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*	

HIGHLIGHTS

Enzymes in search of a function, for polyphenol oxidases (PPOs), described as such, this situation has changed recently. A tyrosinase is involved in betacyanin biosynthesis in common portulaca (see picture) and red beet, and a chalcone-specific PPO is responsible for the formation of aurones in yellow snapdragon flowers.

Angew. Chem. **2001**, *113*, 3907 – 3911

D. Strack,* W. Schliemann* . 3791 – 3794

Bifunctional Polyphenol Oxidases: Novel Functions in Plant Pigment Biosynthesis

Keywords: aurones · biosynthesis · flower pigments · natural products · oxidases · tyrosinases

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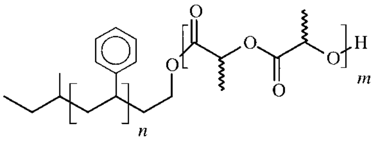
Defined porosity in the low-nanometer range is exhibited by easy-to-modify template materials, which can be prepared from mesoporous polystyrene monoliths. These are readily accessible by a mild hydrolysis reaction of a poly(styrene-*b*-lactic acid) precursor (see picture)



Angew. Chem. **2001**, *113*, 3911 – 3913

M. R. Buchmeiser* .... 3795 – 3797

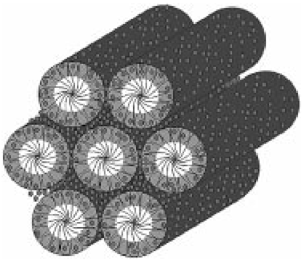
New Ways to Porous Monolithic Materials with Uniform Pore Size Distribution

Keywords: membranes · mesoporous materials · nanostructures · polymers

COMMUNICATIONS

Coordinated water molecules induce the aggregation and self-assembly of the lyotropic liquid crystalline phase formed from non-ionic surfactants $C_nH_{2n+1}(CH_2CH_2O)_mOH$ and transition metal aqua complexes ($[Ni(H_2O)_6](NO_3)_2$, $[Co(H_2O)_6](NO_3)_2$, $[Zn(H_2O)_6](NO_3)_2$, $[Cd(H_2O)_4](NO_3)_2$, and $[Co(H_2O)_6]Cl_2$) into hexagonal (see schematic representation) and/or cubic structures. While the Ni^{II} and Co^{II} complexes undergo recrystallization and phase separation at high complex concentrations, the Zn^{II} and Cd^{II} complexes form cubic phases above metal/surfactant molar ratios of 3.2/1 at room temperature.

Angew. Chem. **2001**, *113*, 3916 – 3919



Ö. Çelik, Ö. Dag* .... 3800 – 3803

A New Lyotropic Liquid Crystalline System: Oligo(ethylene oxide) Surfactants with $[M(H_2O)_n]X_m$ Transition Metal Complexes

Keywords: liquid crystals · mesophases · nanostructures · surfactants · transition metals

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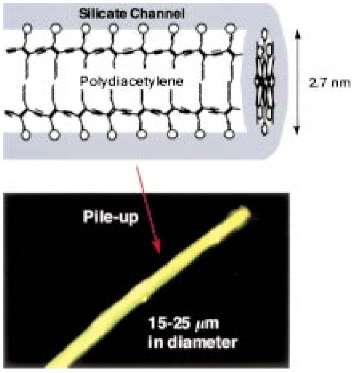
Sticklike silicate materials containing aligned nanodomains of conjugated polymers (see picture) were synthesized by sol – gel-based in situ polymerization of ammonium ion terminated diacetylenic surfactant monomers. Upon photoexcitation at 450 nm, the silicate microsticks emit a yellowish green luminescence centered at 550 nm.

Angew. Chem. **2001**, *113*, 3919 – 3922



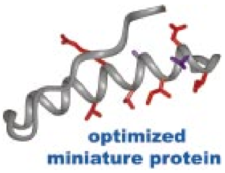
T. Aida,* K. Tajima .... 3803 – 3806

Photoluminescent Silicate Microsticks Containing Aligned Nanodomains of Conjugated Polymers by Sol – Gel-Based In Situ Polymerization

Keywords: luminescence · nanostructures · organic-inorganic hybrid composites · polymerization · sol – gel processes

1433-7851/01/4020-3711 $ 17.50+.50/0

A major challenge for chemical biologists lies in the design of potent and selective ligands for protein surfaces. Here a protein grafting and evolution strategy is used to discover highly potent and specific miniature protein ligands (see picture) for human Bcl-2 and Bcl-X_L. Miniature proteins could be used to dissect, modulate, or analyze a single protein function, irrespective of the other functions the protein may regulate within the proteome.



Angew. Chem. **2001**, *113*, 3922–3925

J. W. Chin, A. Schepartz* . . . 3806–3809

Design and Evolution of a Miniature Bcl-2 Binding Protein

Keywords: apoptosis · protein design · protein–protein interactions · proteins

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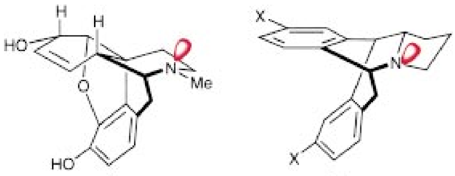
The power of visual imagery can reach Daliesque proportions in the mind's eye of the synthetic chemist. The topologically interesting isopavine nucleus, with an orthogonal orientation of two aryl groups, can be obtained as two diastereomeric structures, depending on the course of a [1,2]-Stevens rearrangement. When viewed as a constrained piperidine, a close spatial relationship with morphine (**1**) becomes apparent. Indeed, tetracyclic isopavine **2** exhibits morphine-like activity toward the human *μ*-opioid receptor.



1 **2**

Angew. Chem. **2001**, *113*, 3926–3929

S. Hanessian,* M. Mauduit . . 3810–3813

Highly Diastereoselective Intramolecular [1,2]-Stevens Rearrangements—Asymmetric Syntheses of Functionalized Isopavines as Morphinomimetics

Keywords: alkaloids · medicinal chemistry · morphine mimetics · rearrangement · synthetic methods

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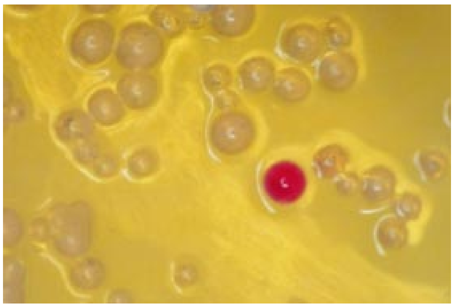
Catalytic beads are readily distinguished from inactive controls in a method which exploits the localizing potential of a gel. A useful variant employs an acid/base indicator to detect the pH change on ester hydrolysis (see picture). Precipitation of the acidified indicator (red) creates an especially strong contrast between active and inactive beads.



Angew. Chem. **2001**, *113*, 3929–3931

M. Müller, T. W. Mathers,
A. P. Davis* 3813–3815

A New Screen for Combinatorial Catalysis; On-Bead Testing in Agarose Gel

Keywords: combinatorial chemistry · enzyme catalysis · high-throughput screening · hydrolysis · supported catalysts

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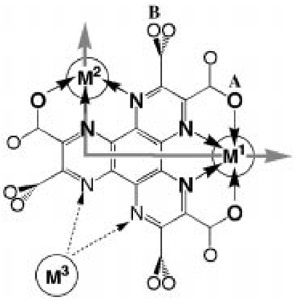
The construction of nanostructured polynuclear metal complexes with cyclic topologies, particularly those containing multifunctional ligands containing π-electronic structures, is of great interest since they can potentially lead to compounds with unusual electrochemical properties. A novel cyclic module with a hexacarboxylate derivative (see picture) is described. The results show that the peripheral substituents not only control the electronic structure, but also influence its mode of coordination.



Angew. Chem. **2001**, *113*, 3933–3935

S. Masaoka, S. Furukawa, H.-C. Chang,
T. Mizutani, S. Kitagawa* . . . 3817–3819

A New Class of Cyclic Hexamer: $[Co_6L_6]^{24-}$ (H_6L = hexaazatriphenylene hexacarboxylic acid)

Keywords: carboxylate ligands · crystal engineering · nanostructures · transition metals

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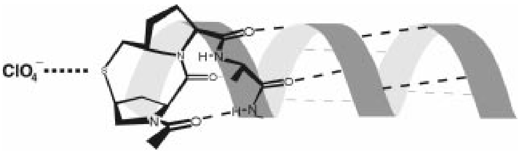
Regiospecific binding of perchlorate ions to the N-terminus of short-chained template-substituted polyalanine sequences (see schematic representation) in water dramatically increases helicity.



Angew. Chem. **2001**, *113*, 3936–3938

W. Maison, R. J. Kennedy,
D. S. Kemp* 3819–3821

Chaotropic Anions Strongly Stabilize Short, N-Capped Uncharged Peptide Helicies: A New Look at the Perchlorate Effect

Keywords: chaotropic anions · circular dichroism · helical structures · peptides

1433-7851/01/4020-3712 $ 17.50+.50/0

Detailed hydrophobicity and lipophilicity charts of the surfaces of crystalline cellulose Iβ are produced by using atomistic molecular dynamics simulations. They reveal patterns of possible sites for the adsorption of hydrophilic and apolar groups of organic adsorbents. The picture shows the simulated distribution of water molecules over a chain of a crystalline 110 surface of cellulose (center; above and below this range lies the bulk water).

Angew. Chem. **2001**, *113*, 3938–3942

O. Biermann, E. Hädicke, S. Koltzenburg, F. Müller-Plathe* 3822–3825

Hydrophilicity and Lipophilicity of Cellulose Crystal Surfaces

Keywords: cellulose · hydration · hydrophobic effect · molecular dynamics · surface chemistry

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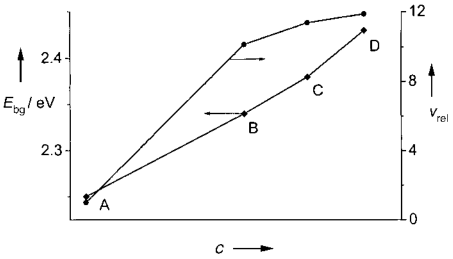
The bandgap of CdS increases with decreasing coverage when CdS is supported on silica (see plot of E_{bg} against CdS concentration c). Likewise the photocatalytic activity of these heterogeneous photocatalysts increases, as illustrated by the relative rate (v_{rel}) of an organic addition reaction. CdS (A, $v_{rel} = 1$), CdS-50/SiO$_2$ (B), CdS-30/SiO$_2$ (C), and CdS-12/SiO$_2$ (D).

Angew. Chem. **2001**, *113*, 3942–3945



H. Weiss, A. Fernandez, H. Kisch* 3825–3827

Electronic Semiconductor–Support Interaction—A Novel Effect in Semiconductor Photocatalysis

Keywords: cadmium sulfide · photocatalysis · photoelectrochemistry · semiconductors

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Indications of the occurrence of mutations can be gained from accurate mass measurements by electrospray ionization mass spectrometry. On-line coupling to liquid chromatography is essential for the application to real samples. By utilizing the coupled method, insertions, deletions, and point mutations are rapidly discovered in DNA restriction fragments and PCR products (see image).

Angew. Chem. **2001**, *113*, 3945–3948

H. Oberacher, P. J. Oefner, W. Parson, C. G. Huber* 3828–3830

On-Line Liquid Chromatography Mass Spectrometry: A Useful Tool for the Detection of DNA Sequence Variation

Keywords: liquid chromatography · mass spectrometry · mutation detection · nucleic acids

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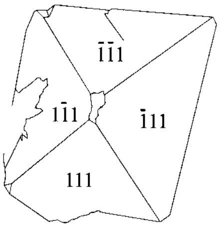
Mimicking recommended! The natural formation conditions of zeolites can be mimicked by treating water-free glass precursors with the composition of the natural zeolite under high-pressure hydrothermal conditions. The picture shows the indexing of the surface of a faujasite crystal obtained in this way. This process can be adapted for the tailored synthesis of zeolites with new properties.

Angew. Chem. **2001**, *113*, 3948–3951



H. Ghobarkar, O. Schäf,* P. Knauth* 3831–3833

Zeolite Synthesis by the High-Pressure Hydrothermal Method: Synthesis of Natural 6-Ring Zeolites with Different Void Systems

Keywords: crystal growth · high-pressure chemistry · hydrothermal synthesis · zeolites

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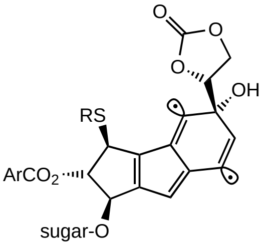
While the general course of the mode of action of the antitumor agent neocarzinostatin (NCS) is clarified, it is still unclear which structural elements are relevant for the high efficacy of NCS. This question and the role of alternatively possible biradicals (see picture) are addressed.

Angew. Chem. **2001**, *113*, 3951–3954



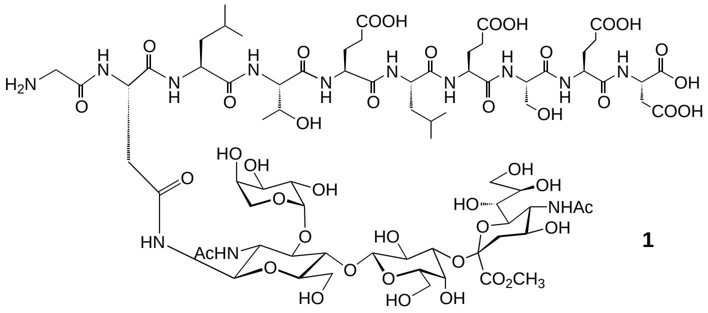
P. W. Musch, B. Engels* 3833–3836

Which Structural Elements Are Relevant for the Efficacy of Neocarzinostatin?

Keywords: ab initio calculations · antibiotics · density functional calculations · DNA cleavage · solvent effects

1433-7851/01/4020-3713 $ 17.50+.50/0

Particularly selective methods are required for the synthesis of arabino sialyl Lewis^x glycopeptides owing to the acid-labile β-arabinopyranoside bond. It is important for the inhibition of cell adhesion that the arabino sialyl Lewis^x glycopeptide **1**, which contains the Gly^{672}–Asp^{681} sequence of the E-selectin Ligand 1 (ESL-1), binds ten times more strongly than sialyl Lewis^x to E-selectin, although it is monovalent and does not contain L-fucose, which is considered essential.



Angew. Chem. **2001**, *113*, 3954–3957

M. Rösch, H. Herzner, W. Dippold,
M. Wild, D. Vestweber,
H. Kunz* 3836–3839

Synthetic Inhibitors of Cell Adhesion: A Glycopeptide from E-Selectin Ligand 1 (ESL-1) with the Arabino Sialyl Lewis^x Structure

Keywords: allyl anchor · E-selectin ligand · glycopeptides · sialyl Lewis^x mimetica · solid-phase synthesis

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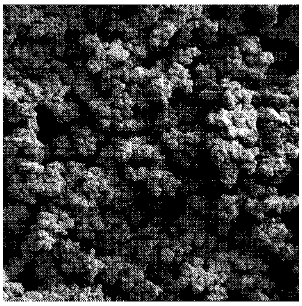
Back to the roots: Ring-opening metathesis polymerization allows the synthesis of monolithic materials, which may be subject to an in situ derivatization with dihydroimidazolium salts through metathesis graft polymerization. This method offers an attractive route to highly reactive, permanently immobilized metathesis initiators. The picture shows an electron microscope image of the microstructure of the monolithic support.



Angew. Chem. **2001**, *113*, 3957–3960

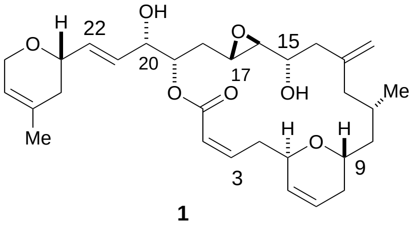
M. Mayr, B. Mayr,
M. R. Buchmeiser* 3839–3842

Monolithic Materials: New High-Performance Supports for Permanently Immobilized Metathesis Catalysts

Keywords: heterogeneous catalysis · metathesis · nanostructures · ring-opening polymerization · ruthenium

---

The microtubule-stabilizing antitumor agent laulimalide (**1**) has been obtained in by new synthetic route. The carbon skeleton was assembled by means of Julia–Kocienski (C16–C17) and Horner–Wadsworth–Emmons (C21–C22) olefinations. Still–Gennari olefination was used for the C2–C3 ring closure. The key step of the synthesis was a regioselective C16–C17 matched Sharpless asymmetric epoxidation.



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Angew. Chem. **2001**, *113*, 3961–3964

J. Mulzer,* E. Öhler* 3842–3846

An Intramolecular Case of Sharpless Kinetic Resolution: Total Synthesis of Laulimalide

Keywords: asymmetric synthesis · chiral pool · epoxidation · macrolides · olefination

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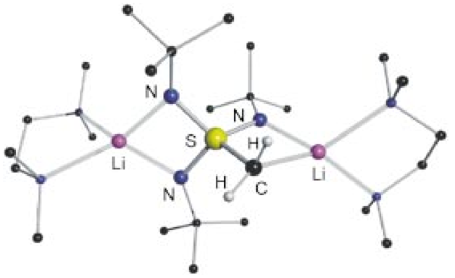
Through isoelectronic replacement of the oxygen atoms in SO_4^{2-} ions by one CH_2 and three N*t*Bu groups one arrives formally at the dianion $H_2CS(NtBu)_3^{2-}$, which has been isolated for the first time in the form of the sulfur(VI) ylide complex $[(tmeda)_2Li_2\{CH_2S(NtBu)_3\}]$ (see structure). Deprotonation of the S-bonded methyl group in the triimidosulfonate $MeS(NtBu)_3^-$ ion provides facile access in good yields. Hydrolysis favors the formation of the triimidosulfate $[\{(tmeda)Li_2[OS(NtBu)_3]\}_3]$ and methane, and not, as one might expect, diimidomethylenesulfate and the amine. tmeda = $Me_2NCH_2CH_2NMe_2$.



Angew. Chem. **2001**, *113*, 3965–3968

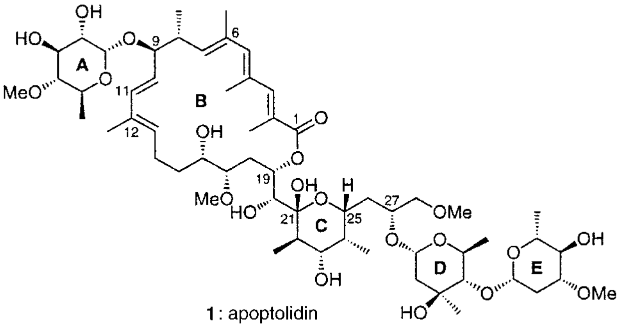
B. Walfort, D. Stalke* 3846–3849

Methylenetriimidosulfate $H_2CS(NtBu)_3^{2-}$—The First Dianionic Sulfur(VI) Ylide

Keywords: bond theory · carbanions · lithium · S ligands · ylides

1433-7851/01/4020-3714 $ 17.50+.50/0

No less than 30 stereogenic elements, a highly unsaturated 20-membered macrocyclic system, four carbohydrate units, and unique biological activity, make the natural occurring apoptolidin (**1**) a challenging synthetic target. The retrosynthetic analysis revealed five key building blocks—three for the construction of the macrolide ring **B** and two prospective pendant saccharide units—which were synthesized in a highly convergent manner and then connected. Apoptolidin's rather labile nature proved particularly challenging in the final deprotection, purification, and characterization procedures.



1: apoptolidin

Angew. Chem. **2001**, *113*, 3968–3972

Angew. Chem. **2001**, *113*, 3972–3976

K. C. Nicolaou,* Y. Li,
K. C. Fylaktakidou, H. J. Mitchell,
H.-X. Wei, B. Weyershausen 3849–3854

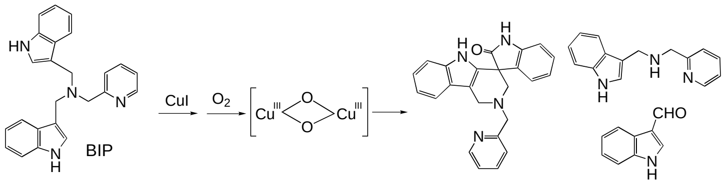
Total Synthesis of Apoptolidin-Part 1: Retrosynthetic Analysis and Construction of Building Blocks

K. C. Nicolaou,* Y. Li,
K. C. Fylaktakidou, H. J. Mitchell,
K. Sugita 3854–3857

Total Synthesis of Apoptolidin-Part 2: Coupling of Key Building Blocks and Completion of the Synthesis

Keywords: apoptolidin · macrolides · natural products · total synthesis

Stabilization of the bis(μ-oxo)dicopper(III) intermediate is achieved by using a bidentate N-donor ligand with pendent indole rings: *N,N*-bis[(3-indolyl)methyl]-*N*-[(2′-pyridyl)methyl]amine (BIP). The intermediate decomposes to give products arising from N-dealkylation and a product with a spiro ring composed of two indole rings (see scheme). This latter product probably results from a radical-coupling reaction.



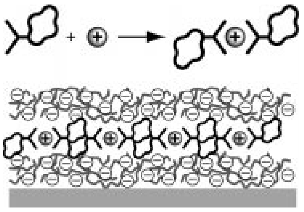
Angew. Chem. **2001**, *113*, 3977–3980

Y. Shimazaki, T. Nogami, F. Tani,
A. Odani, O. Yamauchi* ... 3859–3862

Effects of a Side Chain Aromatic Ring on the Reactivity of Copper(I) Complexes with Dioxygen

Keywords: copper · N ligands · oxidation · radical reactions · structure elucidation

Layer-by-layer deposition of π-assembled arrays of discrete metallo units with aryl tails and polystyrenesulfonate gives structurally well-defined thin films (see schematic representation). The formation of these films, which is controlled by $\pi-\pi$ interactions, metal–ion coordination, and electrostatic interactions, bridges the gap between supramolecular crystal engineering and design of layered materials.



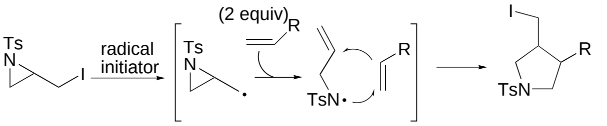
Angew. Chem. **2001**, *113*, 3980–3983

H. Krass, E. A. Plummer, J. M. Haider,
P. R. Barker, N. W. Alcock,
Z. Pikramenou,* M. J. Hannon,*
D. G. Kurth* 3862–3865

Immobilization of π-Assembled Metallo-Supramolecular Arrays in Thin Films: From Crystal-Engineered Structures to Processable Materials

Keywords: crystal engineering · N ligands · pi interactions · supramolecular chemistry · thin films

Functionalized pyrrolidine derivatives are accessible in good yields by radical iodine-transfer [3+2] cycloaddition of electron-rich alkenes with azahomoallyl radicals [Eq. (1)], which were generated by treating iodoaziridine derivatives with radical initiators. Ts = tosyl; 4-methylphenyl sulfonyl



(1)

Angew. Chem. **2001**, *113*, 3983–3985

O. Kitagawa, Y. Yamada, H. Fujiwara, T. Taguchi* 3865–3867

Iodoaziridine Derivatives as Novel Azahomoallyl Radical Precursors for [3+2] Cycloaddition Reactions with Alkenes

Keywords: cycloaddition • nitrogen heterocycles • radical reactions • synthetic methods

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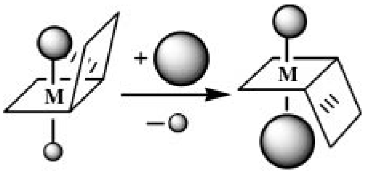
Control of the conformation of the fluorenylidene moiety is achieved through an intramolecular interaction between the fluorenylidene moiety and the axial ligand during the oxidative addition and successive substitution of [Pt^{II}(fm)] to give [Pt^{IV}(X)(X′)(fm)] (fm = 9-fluorenylidenemalonate; see scheme). The conformation of the fm moiety can be effectively induced by the fluorenylidene-philicity of the axial X/X′ ligands, $OOCCH_3 > OCH_3 > OH$.



Angew. Chem. **2001**, *113*, 3986–3988

Y.-A. Lee, O.-S. Jung* 3868–3870

Unusual Fluorenylidene-philic Interactions for Effective Conformational Induction

Keywords: arene ligands • conformation analysis • noncovalent interactions • oxidative addition • platinum

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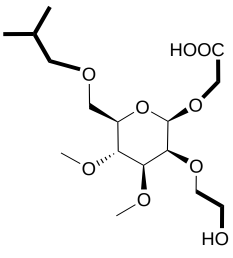
A cyclic peptide role model was used for the design and synthesis of a new class of biologically active and α_4-selective integrin antagonists (e.g. **1**) based on β-D-mannose. These carbohydrate-based peptidomimetics were synthesized to include the functional groups of their cyclic peptide precursors without the redundant amide backbone.



1

Angew. Chem. **2001**, *113*, 3988–3991

J. Boer, D. Gottschling, A. Schuster, B. Holzmann, H. Kessler* .. 3870–3873

Design, Synthesis, and Biological Evaluation of $\alpha_4\beta_1$ Integrin Antagonists Based on β-D-Mannose as Rigid Scaffold

Keywords: carbohydrates • drug research • integrins • peptidomimetics

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The solvent plays a pivotal role in controlling the selectivity of the catalytic hydrogenation of alkenes and alkynes by [$Ru_3(CO)_{12-x}(PPh_3)_x$] ($x = 1$ or 2) with the mechanism varying with the solvent polarity. In polar solvents the reaction proceeds via H_2 addition products based on [$Ru_3(H)(\mu\text{-}H)(CO)_9(PPh_3)_2$], as demonstrated by parahydrogen-induced polarization (PHIP). In nonpolar solvents catalysis by [$RuH_2(CO)_2(PPh_3)$(substrate)], resulting from fragmentation, competes with that by the intact cluster.

Angew. Chem. **2001**, *113*, 3992–3995

D. Blazina, S. B. Duckett,* P. J. Dyson,* J. A. B. Lohman 3874–3877

Direct Comparison of Hydrogenation Catalysis by Intact versus Fragmented Triruthenium Clusters

Keywords: catalysts • cluster compounds • hydrogenation • parahydrogen • ruthenium

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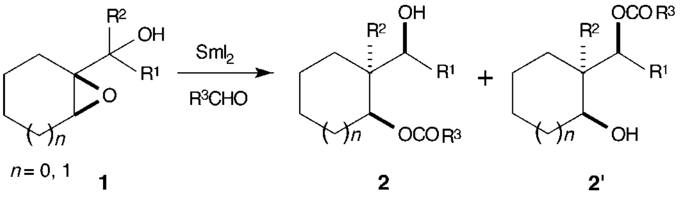
Three contiguous stereocenters are constructed with high diastereoselectivity in a novel samarium-catalyzed tandem reaction of α-hydroxy epoxides **1** to give exclusively the C1,C2-*anti* isomers of **2** and **2′**. This could lead to the development of a general procedure for the diastereoselective construction of 2-quaternary 1,3-diol units.



R^1, R^2: alkyl, aryl; R^3: phenyl, *p*-chlorophenyl

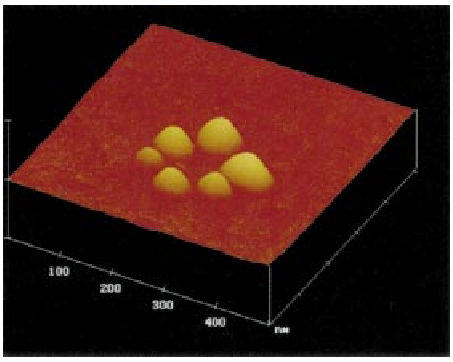
Angew. Chem. **2001**, *113*, 3995–3998

C.-A. Fan, B.-M. Wang, Y.-Q. Tu,* Z.-L. Song 3877–3880

Samarium-Catalyzed Tandem Semipinacol Rearrangement/Tishchenko Reaction of α-Hydroxy Epoxides: A Novel Approach to Highly Stereoselective Construction of 2-Quaternary 1,3-Diol Units

Keywords: alcohols • diastereoselectivity • rearrangement • samarium

A “grafting” method for creating new polymer/V_2O_5/carbon structures with nanodimensions results in materials that are chemically tailored to exhibit fast ion/electron transport. The rate responses are high enough to be of interest in applications such as lithium batteries and supercapacitors, and the concept is applicable to a variety of materials. The picture shows the atomic force microscopy image of V_2O_5/C-PEG nanoparticles on a mica surface. C-PEG = polyethylene glycol functionalized carbon.



Angew. Chem. **2001**, *113*, 3998 – 4002

H. Huang, L. F. Nazar* ..... 3880 – 3884

Grafted Metal Oxide/Polymer/Carbon Nanostructures Exhibiting Fast Transport Properties

Keywords: carbon · conducting materials · nanostructures · organic-inorganic hybrid composites · scanning probe microscopy

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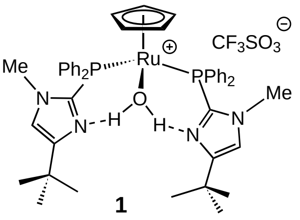
A binding pocket for water is created in **1** by the imidazolyl phosphane ligands and the Ru^{II} center. Compound **1** proves to be an excellent catalyst for a highly selective anti-Markovnikov hydration of terminal alkynes to give aldehydes rather than isomeric ketones under near-neutral conditions (aldehyde-to-ketone ratio up to 1000:1).



Angew. Chem. **2001**, *113*, 4002 – 4005

D. B. Grotjahn,* C. D. Incarvito,
A. L. Rheingold .... 3884 – 3887

Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-Markovnikov Hydration of Terminal Alkynes

Keywords: aldehydes · alkynes · homogeneous catalysis · N,P ligands · ruthenium

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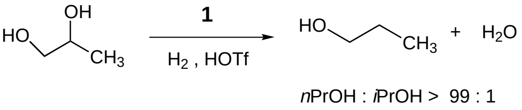
The internal OH group of 1,2-propanediol is selectively removed in the deoxygenation catalyzed by $[\{Cp^*Ru(CO)_2\}_2(\mu\text{-}H)]^+OTf^-$ (**1**, $Cp^* = C_5Me_5$, OTf = trifluoromethanesulfonate; see scheme). This reaction provides a model for deoxygenation of polyols derived from carbohydrates, for use in alternative, biomass-based feedstock applications. An ionic mechanism is proposed that involves the dihydrogen complex $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$.



Angew. Chem. **2001**, *113*, 4005 – 4008

M. Schlaf, P. Ghosh, P. J. Fagan,
E. Hauptman,
R. M. Bullock* .... 3887 – 3890

Metal-Catalyzed Selective Deoxygenation of Diols to Alcohols

Keywords: alcohols · deoxygenation · homogeneous catalysis · hydrido complexes · hydrogenation

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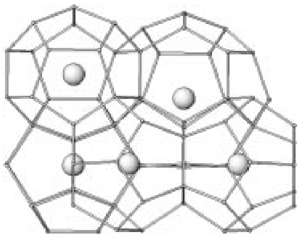
When hyperpolarized xenon is placed in contact with a structure II hydrate of THF, Xe NMR spectroscopy shows that a metastable structure II hydrate of Xe (see picture) forms that decomposes to a structure I Xe hydrate and a mixed structure II hydrate of xenon and THF.



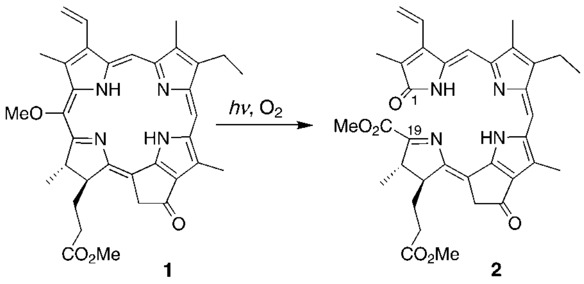
Angew. Chem. **2001**, *113*, 4008 – 4010

I. L. Moudrakovski, C. I. Ratcliffe,
J. A. Ripmeester* .... 3890 – 3892

Probing Transient Hydrate Structures with Hyperpolarized ^{129}Xe NMR Spectroscopy: A Metastable Structure II Hydrate of Xe

Keywords: clathrates · host – guest systems · NMR spectroscopy · phase transitions · xenon

Remarkable selectivity is exhibited in the photooxidation of 20-methoxychlorin methyl ester (**1**) to exclusively yield the C1–C20 bond cleaved product **2**. This selectivity lends strong support to the hypothesis that a hydroxy or equivalent group at C20 directs the C1–C20 bond cleavage that transforms chlorophylls into krill and dinoflagellate luciferins.



Angew. Chem. **2001**, *113*, 4010–4012

G. Topalov, Y. Kishi* 3892–3894

Chlorophyll Catabolism Leading to the Skeleton of Dinoflagellate and Krill Luciferins: Hypothesis and Model Studies

Keywords: chemoselectivity · chlorophyll catabolism · cleavage reactions · photooxidation · porphyrinoids

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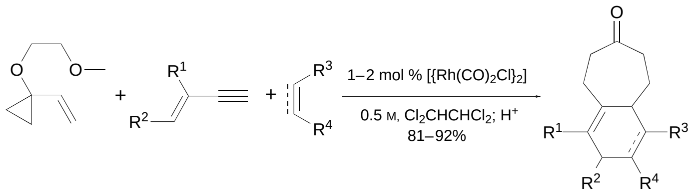
Four new bonds and up to four new stereocenters are formed in the title reactions which allow the conversion of readily available starting materials into complex bicyclo[5.4.0]undecane derivatives (see scheme). The reactions are performed in a single, simple operation that can be conducted on a preparative scale (100 mmol thus far).



Angew. Chem. **2001**, *113*, 4013–4015

P. A. Wender,* G. G. Gamber,
M. J. C. Scanio 3895–3897

Serial [5+2]/[4+2] Cycloadditions: Facile, Preparative, Multi-Component Syntheses of Polycyclic Compounds from Simple, Readily Available Starting Materials

Keywords: chemoselectivity · cycloaddition · enynes · rhodium · tandem reactions

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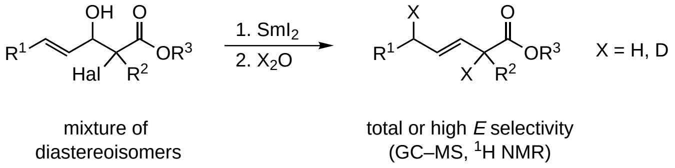
A simple, efficient, highly diastereoselective method for preparing (E)-α,δ-dideuterio-β,γ-unsaturated esters: SmI_2-promoted reduction/elimination of α-halo-β-hydroxy-γ,δ-unsaturated esters in the presence of D_2O (see scheme). This provides the desired products in which the C–C double bond is generated with total or high diastereoselectivity.



Angew. Chem. **2001**, *113*, 4015–4017

J. M. Concellón,* P. L. Bernad,
H. Rodríguez-Solla 3897–3899

Synthesis of Isotopically Labeled (E)-β,γ-Unsaturated Esters with Total or High Diastereoselectivity by Using Samarium Diiodide

Keywords: asymmetric synthesis · deuterium · elimination · reduction · samarium

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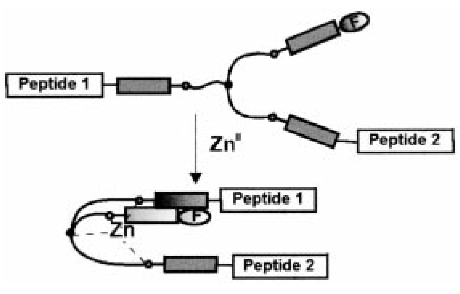
A sevenfold increase in the ability to bind to the dimerization interface of HIV-1 protease is observed by adding a Zn^{II} ion to a tris(aminoethyl)-amine (TREN) templating unit, which bears two peptides with similar sequences as those at the C and N termini of each monomer of the dimeric enzyme (see picture). It is suggested that the metal ion changes the conformation of the putative inhibitor.



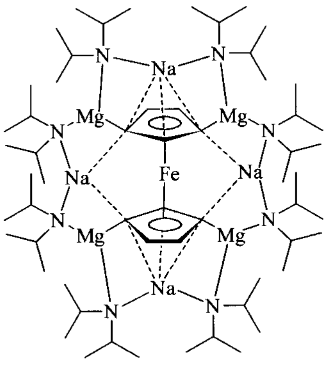
Angew. Chem. **2001**, *113*, 4017–4020

S. Valente, M. Gobbo, G. Licini,*
A. Scarso, P. Scrimin* 3899–3902

Allosteric Regulation of an HIV-1 Protease Inhibitor by Zn^{II} Ions

Keywords: allosterism · enzyme inhibitors · peptides · zinc

Remarkably, four hydrogen atoms have been regioselectively removed from the 1,1′,3,3′-positions of ferrocene in a single reaction leading to the formation of the new macrocyclic host–guest complex $[\{Fe(C_5H_3)_2\}Na_4Mg_4\{iPr_2N\}_8]$ (see picture). This novel addition to the s-block metal inverse crown family possesses a tetrasodium–tetramagnesium amido $(Na_4Mg_4N_8)^{4+}$ ring to complete a series of 8, 12, 16, and 24-membered rings.



W. Clegg, K. W. Henderson,
A. R. Kennedy, R. E. Mulvey,*
C. T. O'Hara, R. B. Rowlings,
D. M. Tooke 3902–3905

Regioselective Tetrametalation of Ferrocene in a Single Reaction: Extension of s-Block Inverse Crown Chemistry to the d-Block

Keywords: alkali metals • alkaline earth metals • amides • crown compounds • ferrocene • host–guest systems

Angew. Chem. **2001**, *113*, 4020–4023

An organic reaction between two populations of vesicles, one containing a nucleophile (blue) and the other an electrophile (red), was examined kinetically (see scheme). By comparing the rates with those of suitable controls, it was demonstrated that the electrophile is transferred during vesicle collisions, and a fast intra-vesicular reaction ensues.

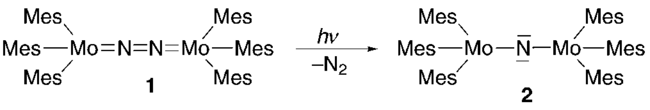
F. M. Menger,* K. L. Caran,
V. A. Seredyuk 3905–3907

Chemical Reaction between Colliding Vesicles

Keywords: colloids • homogeneous catalysis • reaction kinetics • vesicles

Angew. Chem. **2001**, *113*, 4023–4025

Photoinduced cleavage of the residual N–N bond in the dimetallahydrazone **1** (Mes = 2,4,6-$Me_3C_6H_2$) led to a transient monomeric nitrido complex, which reacts further with **1** to form **2**. Compound **1** was synthesized by the reductive arylation of $MoCl_4 \cdot DME$ by MesMgBr under an N_2 atmosphere.



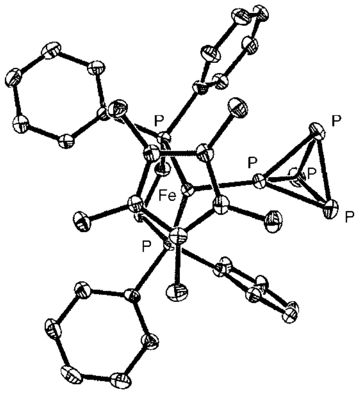
E. Solari, C. Da Silva, B. Iacono,
J. Hesschenbrouck, C. Rizzoli,
R. Scopelliti, C. Floriani* .. 3907–3909

Photochemical Activation of the N≡N Bond in a Dimolybdenum–Dinitrogen Complex: Formation of a Molybdenum Nitride

Keywords: dinitrogen • molybdenum • nitrides • photochemistry

Angew. Chem. **2001**, *113*, 4025–4027

At variance with white phosphorus, the most reactive allotrope of the element, which is unstable and ignites spontaneously in air, the new η^1-*tetrahedro*-tetraphosphorus complexes $[Cp^*M(PR_3)_2(\eta^1\text{-}P_4)]Y$ (M = Fe, Ru; Y = Cl, PF_6, BPh_4, BAr'_4; Cp* = C_5Me_3 the structure of the $[Cp^*Fe(Ph_2PCH_2CH_2PPh_2)(\eta^1\text{-}P_4)]^+$ ion is depicted) exhibit a surprising and unprecedented thermal stability and an astonishing reluctance to react with oxygen and other oxidants.



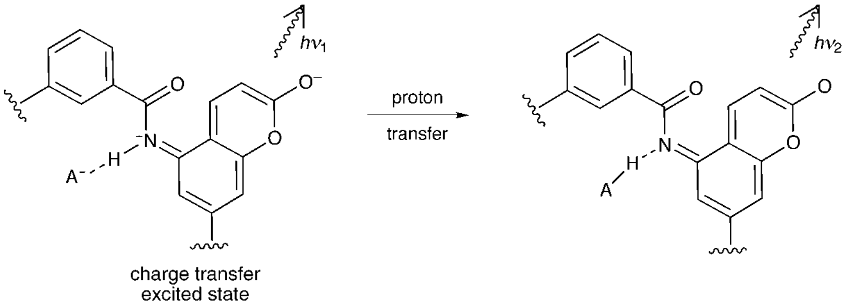
I. de los Rios, J.-R. Hamon, P. Hamon,
C. Lapinte,* L. Toupet, A. Romerosa,
M. Peruzzini* 3910–3912

Synthesis of Exceptionally Stable Iron and Ruthenium η^1-*tetrahedro*-Tetraphosphorus Complexes: Evidence for a Strong Temperature Dependence of M–P_4 π Back Donation

Keywords: cyclopentadienyl ligands • iron • phosphorus • ruthenium • structure elucidation

Angew. Chem. **2001**, *113*, 4028–4030

A macrocycle containing an aminocoumarin fluorophore showed two different fluorescence emission bands on binding with certain anions. Proton transfer from the fluorophore excited state occurred depending on the basicity of the bound anion (see scheme, A$^-$: anion) and this new pathway makes more-sensitive anion sensing possible.



K. Choi, A. D. Hamilton* .. 3912–3915

A Dual Channel Fluorescence Chemosensor for Anions Involving Intermolecular Excited State Proton Transfer

Angew. Chem. 2001, 113, 4030–4033

Keywords: anions · host–guest systems · molecular recognition · sensors

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

* Author to whom correspondence should be addressed

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