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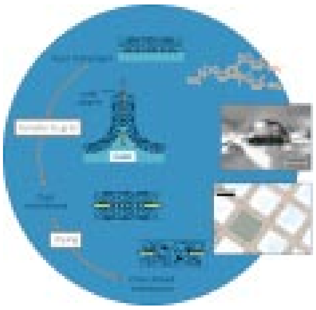
Pages 2557–2724

COVER PICTURE

The cover picture shows nanometer-thin elastomeric membranes made from polyisobutene star polymers with ionic head groups. Spreading of the polymers onto a water surface yields fluid monolayers. These can be transferred to cover openings in solid substrates. After transfer, the ionic head groups aggregate, crosslink the membrane, and thus give rise to elastomeric properties. For example applying a small overpressure from one side gives rise to comparatively large, reversible deformations. These elastomeric membranes could be used in micromechanical devices such as membrane pumps and valves. More details on these membranes are reported by F. Mallwitz and W. Goedel on pages 2645 ff.



REVIEWS

Contents

The science of serendipity: the accidental use of a hypercatalytic amount of a Ziegler–Natta catalyst gave polyacetylene films, such as the one shown in the transmission electron micrograph. This “mishap” opened the way to new conducting polymers, (legal) doping, and the award of the Nobel prize for chemistry.

Angew. Chem. **2001**, *113*, 2642–2648

H. Shirakawa* 2574–2580

The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture)

Keywords: chemical doping · conducting materials · Nobel lecture · polyacetylene · Ziegler–Natta

Plastic silicon chips? Conducting polymers combine the properties of plastics, such as flexibility and processing from solution with conductivity in the metallic or semiconducting regimes. In conjunction with the technique of "line patterning" which allows conducting polymers to be deposited in patterns that are simply printed out on an overhead transparency by a standard office laser printer, liquid crystal displays and field-effect transistors (such as the one shown) can be fabricated, not in the clean room or laboratory, but in the office!

Angew. Chem. **2001**, *113*, 2649 – 2659

Keywords: conducting materials · liquid crystals · nano-electronics · Nobel lecture · polymers

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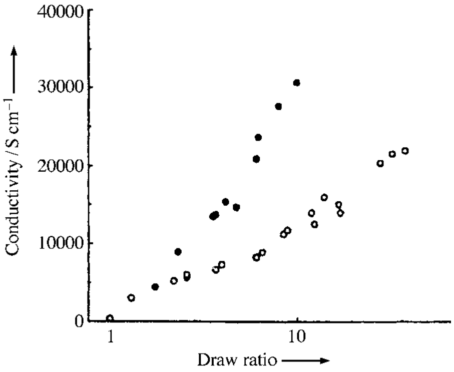
Nobel plastic! Conducting polymers are a new generation of materials. They display the electronic and optical properties of metals or semiconductors as well as the attractive mechanical properties and processibility of polymers. The figure shows the electrical conductivity of iodine-doped polyacetylenes as a function of the draw ratio (●: thin film 3 – 5 μm thick, ○: 20 – 30 μm thick).

Angew. Chem. **2001**, *113*, 2660 – 2682



Keywords: chemical doping · conducting materials · Nobel lecture · polyacetylene · solid-state physics

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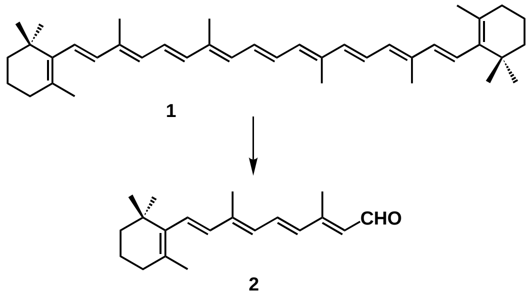
VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (that 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

Targeting Molecular Recognition: Exploring the Dual Role of Functional Pseudoprolines in the Design of SH3 Ligands	G. Tuchscherer,* D. Grell, Y. Tatsu, P. Durieux, J. Fernandez-Carneado, B. Hengst, C. Kardinal, S. Feller*	◆
Synthesis of the C1 – C13 Fragment of Kendomycin: Atropisomerism around a C-Aryl Glycosidic Bond	H. J. Martin,* M. Drescher, H. Kählig, S. Schneider, J. Mulzer*	
$[NdI_2(thf)_5]$: The First Crystallographically Authenticated Divalent Neodymium Complex	M. N. Bochkarev*, I. L. Fedushkin, S. Dechert, A. A. Fagin, H. Schumann*	
From Split-Pool Libraries to Spatially Addressable Microarrays and Its Application to Functional Proteomic Profiling	N. Winssinger, J. L. Harris, B. J. Backes, P. G. Schultz*	

Seeing things as they really are: The enzyme catalyzing the central cleavage of β-carotene (**1**) to retinal (**2**) is not, as previously thought, a dioxygenase. Incubation of the substrate analogue α-carotene in the presence of highly enriched $^{17}O_2$ and $H_2{}^{18}O$ revealed a monooxygenase mechanism.



Angew. Chem. **2001**, *113*, 2684–2687

M. G. Leuenberger, C. Engeloch-Jarret, W.-D. Woggon* 2614–2617

The Reaction Mechanism of the Enzyme-Catalyzed Central Cleavage of β-Carotene to Retinal

Keywords: carotenoids · cleavage reactions · enzyme catalysis · isotopic labeling · oxidation · reaction mechanisms

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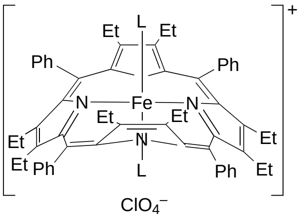
The field strength of the axial ligands determines the spin state of saddled iron(III) porphyrin complexes (see picture). Strong axial ligands (L), such as imidazole and 4-dimethylaminopyridine, lead to the formation of complexes with a pure $S = 1/2$ state, while weak ligands, such as THF, give complexes with a pure $S = 3/2$ state. Intermediate strength ligands, such as pyridine and 4-cyanopyridine, give complexes that show a novel spin crossover between the $S = 1/2$ and $S = 3/2$ states.



Angew. Chem. **2001**, *113*, 2687–2690

T. Ikeue, Y. Ohgo, T. Yamaguchi, M. Takahashi,* M. Takeda, M. Nakamura* 2617–2620

Saddle-Shaped Six-Coordinate Iron(III) Porphyrin Complexes Showing a Novel Spin Crossover between $S = 1/2$ and $S = 3/2$ Spin States

Keywords: iron · magnetic properties · Moessbauer spectroscopy · porphyrinoids · spin crossover

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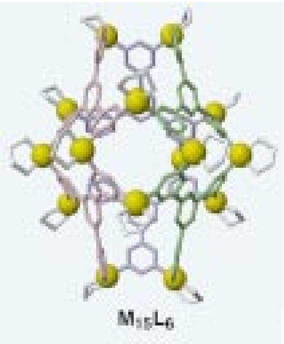
Only one positional isomer is obtained from the assembly of 21 small components. A triangular molecular panel with five coordination sites is assembled upon complexation with $[Pd^{II}(en)]$ (en = ethylenediamine) into a unique $M_{15}L_6$ hexahedral coordination capsule (see X-ray structure). The capsule can encapsulate/exchange organic guests reversibly through the clefts at the nonbinding sites of the capsule.



Angew. Chem. **2001**, *113*, 2690–2692

K. Umemoto, H. Tsukui, T. Kusukawa, K. Biradha, M. Fujita* 2620–2622

Molecular Paneling by Coordination: An $M_{15}L_6$ Hexahedral Molecular Capsule having Clefts for Reversible Guest Inclusion

Keywords: host–guest systems · molecular recognition · palladium · self-assembly

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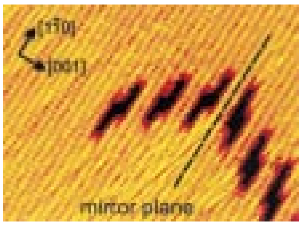
Pronounced surface restructuring leads to the formation of chiral kink sites (see scanning tunneling microscopy image) when a chiral molecular overlayer (2,5,8,11,14,17-hexa-(*tert*-butyl)decacyclene) is adsorbed onto an extended, flat metal surface (Cu{110}). The process is proposed to happen as a result of the adsorbed molecule inducing chirality in the achiral surface.



Angew. Chem. **2001**, *113*, 2693–2696

M. Schunack, E. Lægsgaard, I. Stensgaard, I. Johannsen, F. Besenbacher* 2623–2626

A Chiral Metal Surface

Keywords: chirality · interfaces · monolayers · nanostructures · scanning probe microscopy

1433-7851/01/4014-2561 $ 17.50+.50/0

A series of hydrosoluble dendrimers has been synthesized by capping phosphorus-containing dendrimers with hydrophilic end groups. These dendrimers form aqueous rigid gels at very low concentration (ca. 1.5% per weight; see picture), which allows, for example, confinement of acids or metals. The structure of the gels has been investigated by freeze-fracture electron microscopy.

Angew. Chem. **2001**, *113*, 2696–2699

C. Marmillon, F. Gauffre,
T. Gulik-Krzywicki, C. Loup,
A.-M. Caminade,* J.-P. Majoral,*
J.-P. Vors, E. Rump 2626–2629

Organophosphorus Dendrimers as New Gelators for Hydrogels

Keywords: dendrimers · gels · phosphorus · polycations · supramolecular chemistry

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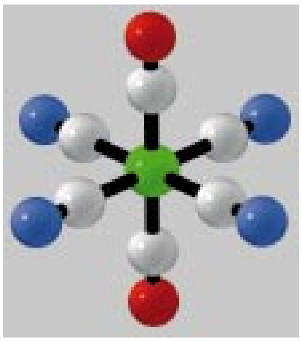
In 1887, more than a century after the synthesis of $[Fe^{II}(CN)_6]^{4-}$, the complex $[Fe^{II}(CN)_5(CO)]^{3-}$, in which a CN^- ligand is replaced by CO, was reported. It has taken an additional century for the synthesis of the complex in which a second CN^- ligand is substituted by CO: *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$ (structure shown). Remarkably, this anion is prepared by the simple reaction of $FeCl_2$ with NaCN and CO in water. $[Fe(CN)_x(CO)_y]$ complexes are of interest as models for the active site of hydrogenase enzymes.



Angew. Chem. **2001**, *113*, 2699–2701

J. Jiang, S. A. Koch* 2629–2631

trans-$[Fe(CN)_4(CO)_2]^{2-}$, a 21st Century [Fe(CN)(CO)] Compound

Keywords: bioinorganic chemistry · carbonyl complexes · C ligands · cyanides · iron

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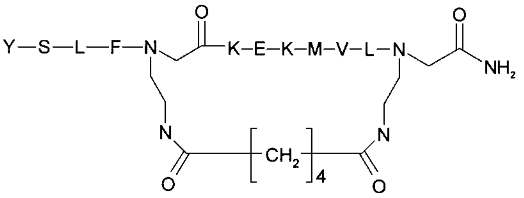
Effective structural mimics of a functionally important epitope from the malarial Merozoite Surface Protein-1 (MSP-1) include N-backbone cyclic peptides such as **1**. They mimic the interaction of MSP-1 with human erythrocytes and can be used to induce parasite-specific monoclonal antibodies.



1

Angew. Chem. **2001**, *113*, 2701–2706

E. Lioy,* J. Suarez, F. Guzmàn,
S. Siegrist, G. Pluschke,
M. E. Patarroyo* 2631–2635

Synthesis, Biological, and Immunological Properties of Cyclic Peptides from *Plasmodium Falciparum* Merozoite Surface Protein-1

Keywords: antibodies · cyclopeptides · ligand–receptor interactions · malaria · peptides

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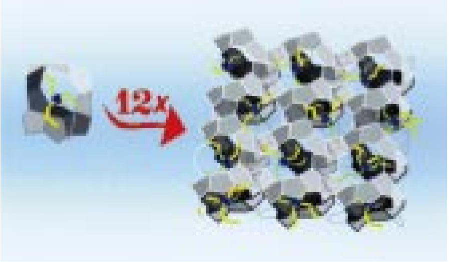
Tetrapropylammonium (TPA)-containing precursors are the building blocks in the crystallization of silica. In the first steps slab-shaped silicalite nanoparticles are formed by ordered combination of the precursors (see picture). These nanoslabs have MFI-type zeolite framework topology and play a key role in TPA-ion-mediated zeolite crystallization from monomeric and polymeric silica sources.



Angew. Chem. **2001**, *113*, 2707–2710

C. E. A. Kirschhock, V. Buschmann,
S. Kremer, R. Ravishankar,
C. J. Y. Houssin, B. L. Mojet,
R. A. van Santen, P. J. Grobet,
P. A. Jacobs, J. A. Martens* . 2637–2640

Zeosil Nanoslabs: Building Blocks in nPr_4N^+-Mediated Synthesis of MFI Zeolite

Keywords: aggregation · host–guest systems · silicates · zeolites

1433-7851/01/4014-2562 $ 17.50+.50/0

A new family of chromogenic ionophores for anion sensing has been developed with 1,3,5-triarylpent-2-en-1,5-diones. These species form yellow solutions that undergo a color change to magenta in the presence of certain inorganic ions or nucleotides, depending on the derivative. The reaction with ATP is particulary remarkable and therefore these compounds are chromogenic reagents for "naked-eye" sensing of ATP. The picture shows the color changes induced on one derivative in the presence of GMP, ADP, and ATP (from left to right).

Angew. Chem. **2001**, *113*, 2710 – 2713

F. Sancenón, A. B. Descalzo,
R. Martínez-Máñez,* M. A. Miranda,
J. Soto .... 2640 – 2643

A Colorimetric ATP Sensor Based on 1,3,5-Triarylpent-2-en-1,5-diones

Keywords: chromophores · cyclization · ketones · nucleotides · sensors

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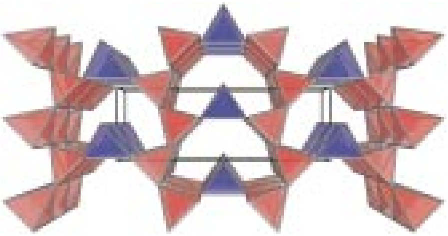
Extreme reaction conditions lead to the synthesis of γ-P_3N_5. Its crystal structure (see picture), unlike that of the normal pressure modification α-P_3N_5, is not exclusively built from PN_4 tetrahedra, but from both PN_4 tetrahedra (blue) and tetragonal PN_5 pyramids (red). A tetragonal PN_5 pyramid structure element has not been observed previously.

Angew. Chem. **2001**, *113*, 2713 – 2716



K. Landskron, H. Huppertz, J. Senker,
W. Schnick* .... 2643 – 2645

High-Pressure Synthesis of γ-P_3N_5 at 11 GPa and 1500 °C in a Multianvil Assembly: A Binary Phosphorus(v) Nitride with a Three-Dimensional Network Structure from PN_4 Tetrahedra and Tetragonal PN_5 Pyramids

Keywords: high-pressure chemistry · nitrides · phase transitions · phosphorus · solid-state structures

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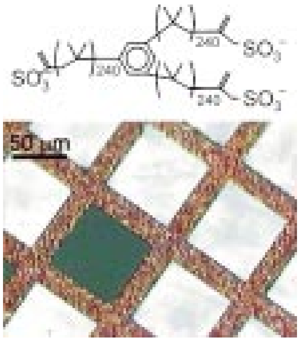
Spreading a hydrophobic liquid star polymer with ionic head groups and transferring the resulting monomolecular layers to solid substrates with holes provides access to ultrathin, freely suspended elastomeric membranes (see picture), which are stable for at least several months.

Angew. Chem. **2001**, *113*, 2716 – 2718



F. Mallwitz,
W. A. Goedel* .... 2645 – 2647

Physically Cross-Linked Ultrathin Elastomeric Membranes

Keywords: membranes · polymers · surface chemistry · surfactants · thin films

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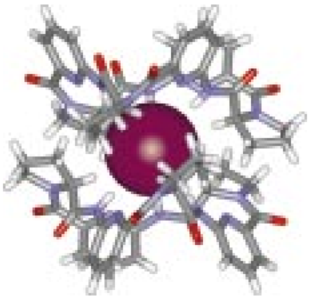
A neutral receptor that binds anions by hydrogen bonds even in water is the cyclopeptide reported in this article. This property results from the particular structure of the complex in which the anions are effectively shielded from the surrounding solvent, as can be seen in the iodide complex shown.

Angew. Chem. **2001**, *113*, 2722 – 2725

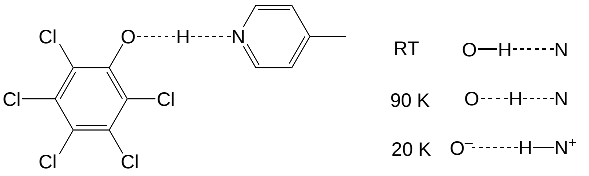


S. Kubik,* R. Goddard, R. Kirchner,
D. Nolting, J. Seidel .... 2648 – 2651

A Cyclic Hexapeptide Containing L-Proline and 6-Aminopicolinic Acid Subunits Binds Anions in Water

Keywords: anion receptors · conformation analysis · cyclopeptides · supramolecular chemistry

Within a range of 0.1 Å, the H atom in the O–H–N hydrogen bond of the adduct 4-methylpyridine · pentachlorophenol could be shifted by a simple adjustment of temperature (see scheme). At approximately 90 K the H atom is exactly centered between the O and the N atoms, as could be shown by stepwise monitoring by using variable-temperature single-crystal neutron diffraction.



Angew. Chem. **2001**, *113*, 2728–2731

T. Steiner,* I. Majerz,*
C. C. Wilson* 2651–2654

First O–H–N Hydrogen Bond with a Centered Proton Obtained by Thermally Induced Proton Migration

Keywords: hydrogen bonds · neutron diffraction · proton transfer · structure elucidation

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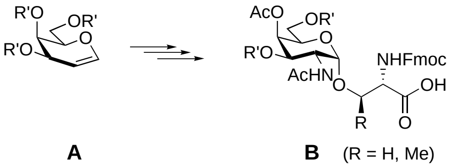
Base-catalyzed glycosylations provide the basis for a new and general entry to the synthesis of mucin-type O-glycans. The desired α-linked 2-acetamidoglycosyl amino acids **B** are accessible selectively starting from glycals of type **A**. Fmoc = 9-fluorenylmethoxycarbonyl.



Angew. Chem. **2001**, *113*, 2718–2721

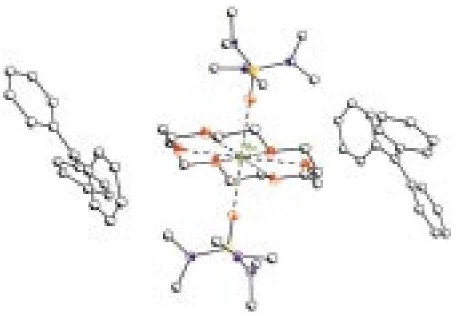
G. A. Winterfeld,
R. R. Schmidt* 2654–2657

Nitroglycal Concatenation: A Broadly Applicable and Efficient Approach to the Synthesis of Complex O-Glycans

Keywords: glycals · glycopeptides · glycosidations · Michael additions · mucins

---

Differences in anion basicity seem to be key for the formation of the first charge-separated barium triphenylmethanide (see structure) versus a novel heteroleptic vinyl ether which results from cleavage of the attendant [18]crown-6. Ba: green; O: red; P: yellow; N: blue.



Angew. Chem. **2001**, *113*, 2732–2734

J. S. Alexander,
K. Ruhlandt-Senge* 2658–2660

Barium Triphenylmethanide: An Examination of Anion Basicity

Keywords: alkaline earth metals · carbanions · ion pairs · triphenylmethane

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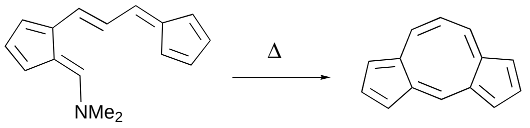
14π-Electrocyclization across the two pentafulvenoid moieties of pentafulvene **1** occurs upon heating to provide dicyclopenta[*a*,*d*]cyclooctene **2** [Eq. (1)]. The nonalternant hydrocarbon **2** shows diatropic character and a distinctive absorption spectrum with the longest wavelength maximum at 767 nm.



(1)

1 **2**

Angew. Chem. **2001**, *113*, 2734–2736

M. Oda,* Y. Sakamoto, T. Kajioka,
T. Uchiyama, R. Miyatake,
S. Kuroda* 2660–2662

Dicyclopenta[*a*,*d*]cyclooctene:
A [14]Annulene Containing Two Zero-Atom Cross-Links

Keywords: annulenes · aromaticity · density functional calculations · electrocyclic reactions · hydrocarbons

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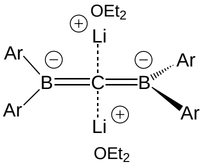
Deviations of up to 36° from the orthogonality of the planes of the terminal B atoms of the allene skeleton and their neighbors (*ipso*-C atoms) are observed in tetraaryl-1,3-diborataallenes of contact-ion triples **1**. The unusual geometries are caused by steric hindrance between *ortho*-methyl groups, which is induced by interactions of the lithium counterions with the π electrons of the aryl substituents, as well as by small barriers to planarization of 1,3-diborataallenes. Ar = for example, 2,3,5,6-tetramethylphenyl.



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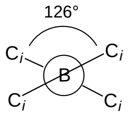

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Angew. Chem. **2001**, *113*, 2725–2728

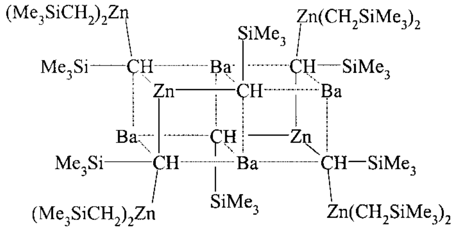
Y. Sahin, M. Hartmann, G. Geiseler,
D. Schweikart, C. Balzereit, G. Frenking,
W. Massa, A. Berndt* 2662–2665

Nonorthogonal Dilithium-1,3-biborataallenes Containing Planar-Tetracoordinate Carbon Atoms

Keywords: anions · boron · coordination chemistry · density functional calculations · steric hindrance

1433-7851/01/4014-2564 $ 17.50+.50/0

Transmetalations of zincates succeed only after activation of the barium metal. Dialkylbarium, the initial product, metalates the zincate anions which are still present in solution and leads to the formation of tetraanionic tris(zincate) ligands, which sterically shield the Ba–C bonds of a $Ba_4Zn_2C_6$ cage (see structure).



Angew. Chem. **2001**, *113*, 2736–2739

M. Westerhausen,* C. Gückel,
P. Mayer 2666–2668

Synthesis and Structure of a Dimeric Alkyldibariumtriszincate with a Tetraanionic Triszincate Ligand and a Unique Central $Ba_4Zn_2C_6$ Moiety

Keywords: barium • cage compounds • metalation • polyanions • zinc

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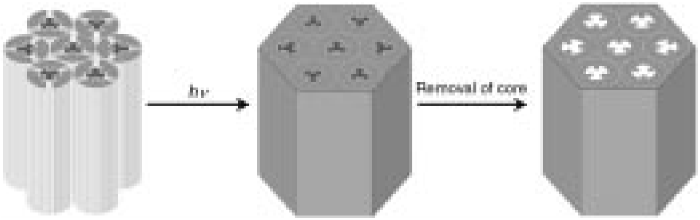
Hydrogen-bonding interactions between a benzotri(imidazole) derivative and a polymerizable alkoxybenzoic acid result in the formation of a supramolecular hexagonal columnar liquid crystal. Light-induced polymerization followed by removal of the benzotri(imidazole) core produces a porous polymer with hexagonal channels (see scheme).



Angew. Chem. **2001**, *113*, 2741–2743

H.-K. Lee, H. Lee, Y. H. Ko, Y. J. Chang,
N.-K. Oh, W.-C. Zin,
K. Kim* 2669–2671

Synthesis of a Nanoporous Polymer with Hexagonal Channels from Supramolecular Discotic Liquid Crystals

Keywords: hydrogen bonds • liquid crystals • polymers • supramolecular chemistry • template synthesis

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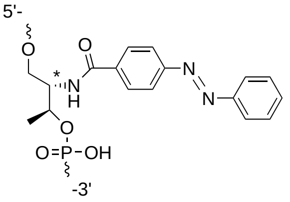
A drop in melting point of 21.5°C is induced by the UV-photolytic *trans→cis* isomerization of the duplex formed between an oligonucleotide bearing two D-threoninol-tethered azobenzene moieties (see picture) in the side chain and its complementary counterpart. On irradiation with visible light, the dissociated single-stranded oligonucleotides regenerate the duplex.



Angew. Chem. **2001**, *113*, 2743–2745

H. Asanuma,* T. Takarada, T. Yoshida,
D. Tamaru, X. Liang,
M. Komiyama* 2671–2673

Enantioselective Incorporation of Azobenzenes into Oligodeoxyribonucleotide for Effective Photoregulation of Duplex Formation

Keywords: azo compounds • DNA structures • isomerization • nucleotides • photochemistry

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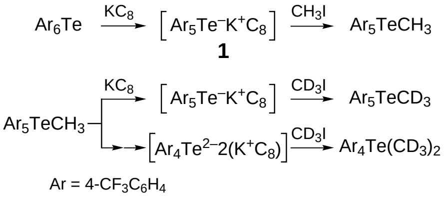
The potassium ion intercalated in graphite results in unique reactivity of $Ar_5Te^-K^+C_8$ (**1**), formed by cleavage of one of the Te–C(Ar) bonds of Ar_6Te (see scheme) by KC_8. Thus, **1** reacted quantitatively with CH_3I to give Ar_5TeCH_3, which was not obtainable from $Ar_5Te^-Li^+$. The Te–CH_3 bond of Ar_5TeCH_3 is cleaved in preference to the Te–C(Ar) bonds, and formation of $Ar_4Te(CD_3)_2$ suggests the intermediacy of the hypervalent dianion Ar_4Te^{2-}.

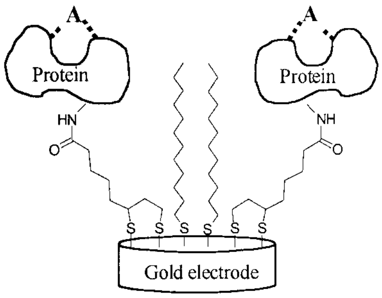


Angew. Chem. **2001**, *113*, 2746–2748

M. Miyasato, M. Minoura,
K.-y. Akiba* 2674–2676

Cleavage of Tellurium–Carbon Bonds of Hexavalent Organotellurium Compounds by Potassium Graphite

Keywords: cleavage reactions • hypervalent compounds • intercalation • tellurium



Sensitive repressors: The conformational change that occurs in the *lac* repressor protein when it binds to an inducer molecule has been used to develop a biosensor that permits the detection of the corresponding operator sequence or specific inducer molecules. A capacitive signal transducer was used to translate the conformational change of the *lac* repressor protein, covalently immobilized on a gold electrode (see schematic representation, A = bound inducer molecule or DNA), into a measurable signal.

Angew. Chem. **2001**, *113*, 2748–2750

I. Bontidean, A. Kumar, E. Csöregi,
I. Yu. Galaev,
B. Mattiasson* 2676–2678

Highly Sensitive Novel Biosensor Based on an Immobilized *lac* Repressor

Keywords: biosensors · capacitance measurement · DNA recognition · proteins

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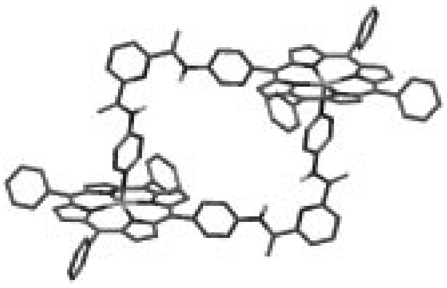

Reversible zinc–pyridine coordination and hydrogen-bonding interactions have been used to assemble a [2]rotaxane from three components. Cooperativity in the macrocyclization process that results in the porphyrin dimer (see picture) makes the system exceptionally stable. However, the kinetic lability of the zinc–porphyrin interaction means the dimer is in dynamic equilibrium with its monomer, and this has been exploited in the construction of a [2]rotaxane.

Angew. Chem. **2001**, *113*, 2750–2754

C. A. Hunter,* C. M. R. Low,
M. J. Packer, S. E. Spey, J. G. Vinter,
M. O. Vysotsky, C. Zonta ... 2678–2682

Noncovalent Assembly of [2]Rotaxane Architectures

Keywords: hydrogen bonds · noncovalent interactions · porphyrinoids · rotaxanes · supramolecular chemistry

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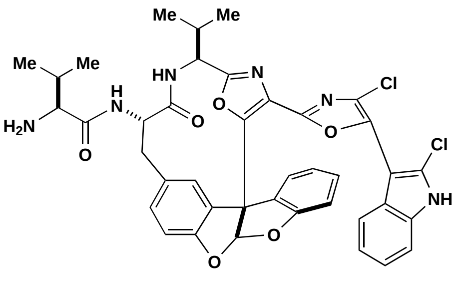

1

One bond and a water molecule separate title compound **1** from the potently bioactive peptide metabolite diazonamide A. Compositionally similar, yet topographically distinct, diazonamide A and **1** are both toxic towards cultured human cancer cells although the mechanisms underlying their actions likely differ. The quest towards completely synthetic diazonamides continues.

Angew. Chem. **2001**, *113*, 2754–2757

J. Li, X. Chen, A. W. G. Burgett,
P. G. Harran* 2682–2685

Synthetic seco Forms of (−)-Diazonamide A

Keywords: antitumor agents · fluorescence spectroscopy · natural products · nitrogen heterocycles · transesterification

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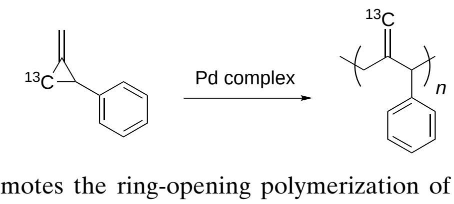


Selective 2,1-insertion of the monomer and subsequent elimination of the β-carbon atom of the growing polymer end is proposed as a new mechanism for polymer synthesis that involves ring opening of the monomer. A palladium complex promotes the ring-opening polymerization of 1-methylene-2-arylcyclopropanes to afford polymers with a vinylidene group in each monomer unit (see scheme).

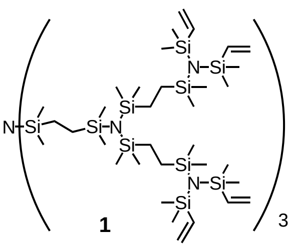
Angew. Chem. **2001**, *113*, 2757–2760

D. Takeuchi, S. Kim,
K. Osakada* 2685–2688

Ring-Opening Polymerization of 1-Methylene-2-phenylcyclopropane Catalyzed by a Pd Complex To Afford Regioregulated Polymers

Keywords: cyclopropanes · N ligands · palladium · polymers · ring-opening polymerization

The controlled synthesis of nematic nanophase-separated materials poses an attractive synthetic challenge. The use of carbosilazane multipodes and dendrimers (such as **1**) in conjunction with laterally attached mesogens allows the systematic investigation of the structure–property relationships of room-temperature nematic liquid crystals.



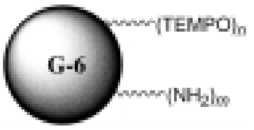
R. Elsässer, G. H. Mehl,* J. W. Goodby, M. Veith 2688–2690

Nematic Dendrimers Based on Carbosilazane Cores

Keywords: dendrimers • liquid crystals • silicon

Angew. Chem. **2001**, *113*, 2760–2762

Sixth-generation PAMAM dendrimers labeled with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, shown schematically) have been synthesized and are shown to reoxidize EPR-silent hydroxylamines to EPR-active nitroxides. Therefore these dendrimers are potential TEMPO free radical life supporters for EPR imaging.



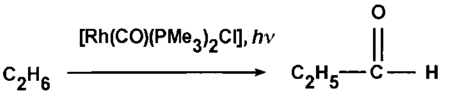
A. T. Yordanov, K.-i. Yamada, M. C. Krishna, J. B. Mitchell, E. Woller, M. Cloninger, M. W. Brechbiel* 2690–2692

Spin-Labeled Dendrimers in EPR Imaging with Low Molecular Weight Nitroxides

Keywords: dendrimers • EPR spectroscopy • oxidation • radicals • reduction

Angew. Chem. **2001**, *113*, 2762–2764

Feasible photocatalysis: The rhodium catalyst [Rh(CO)(PMe$_3$)$_2$Cl] photochemically transforms ethane to propionaldehyde in single-phase mixtures of ethane and in carbon dioxide/ethane single phases [Eq. (1)]. A side reaction of carbon dioxide with the catalyst to give OPMe$_3$ and [Rh(CO)$_2$(PMe$_3$)Cl] or [Rh$_2$(CO)$_2$(PMe$_3$)$_2$(μ-Cl)$_2$] has also been observed.



$$C_2H_6 \xrightarrow{[Rh(CO)(PMe_3)_2Cl],\ h\nu} C_2H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \qquad (1)$$

Angew. Chem. **2001**, *113*, 2764–2766

T. E. Bitterwolf,* D. Lukmanova Kline, J. C. Linehan, C. R. Yonker, R. S. Addleman 2692–2694

Photochemical Carbonylation of Ethane under Supercritical Conditions

Keywords: carbonylation • photocatalysis • photochemistry • rhodium • supercritical fluids

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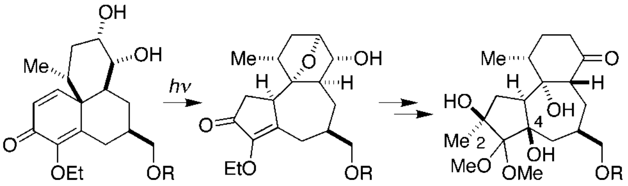
Light as a reagent: A highly functionalized structure that serves as a daphnane template can be formed by the photorearrangement of a 2,5-cyclohexadienone subunit within a complex tricyclic ring system (see scheme). The chemistry we describe should not only find use in the total synthesis of resiniferatoxin and related daphnanes, but should also provide useful templates for access to complex analogues.



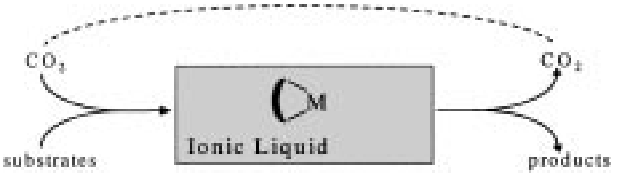
Angew. Chem. **2001**, *113*, 2766–2769

S. R. Jackson, M. G. Johnson, M. Mikami, S. Shiokawa, E. M. Carreira* 2694–2697

Rearrangement of a Tricyclic 2,5-Cyclohexadienone: Towards a General Synthetic Route to the Daphnanes and (+)-Resiniferatoxin

Keywords: photochemistry • rearrangement • synthesis design • synthetic methods

A new immobilization scheme for enantioselective catalysts was developed by using a combination of ionic liquids and compressed CO_2. Under continuous flow conditions, stable conversion and asymmetric induction was achieved over more than 60 h in the enantioselective Ni-catalyzed hydrovinylation of styrene. While the ionic liquid dissolves and activates the organometallic catalyst in a tuneable manner, the presence of compressed CO_2 greatly facilitates mass transfer and gives easy access to continuous processes (see the schematic representation).



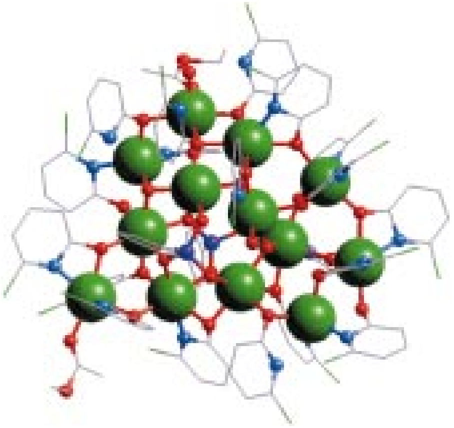
Angew. Chem. **2001**, *113*, 2769–2771

A. Bösmann, G. Franciò, E. Janssen,
M. Solinas, W. Leitner,*
P. Wasserscheid* 2697–2699

Activation, Tuning, and Immobilization of Homogeneous Catalysts in an Ionic Liquid/Compressed CO_2 Continuous-Flow System

Keywords: carbon dioxide · enantioselectivity · homogeneous catalysis · ionic liquids · supercritical fluids

Addition of a coligand in reactions of phosphonates with salts of late 3d metals can lead to more soluble and tractable materials, such as the $\{Co_{13}\}$ cage shown (Co: green; P: purple). The structure contains two central $PhPO_3^{2-}$ ligands, surrounded by a hexanuclear cobalt helix, capped by seven further cobalt sites.



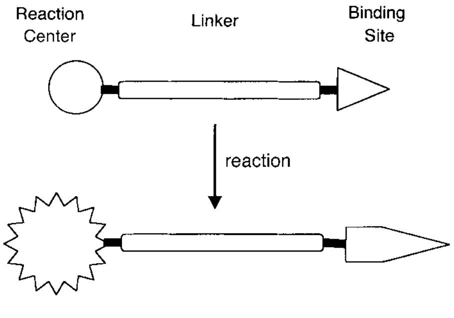
Angew. Chem. **2001**, *113*, 2772–2775

E. K. Brechin, R. A. Coxall, A. Parkin,
S. Parsons, P. A. Tasker,*
R. E. P. Winpenny* 2700–2703

Polymetallic Cobalt and Manganese Cages with Phosphinate and Phosphonate Ligands

Keywords: cluster compounds · cobalt · phosphonate ligands · P ligands

Signal enhancement from a reaction center to a hydrogen-bonding site occurs when they are separated by an azo linker (see schematic representation). A computational study has shown that the binding of ammonia to a pyrrole unit in an iminium compound increases as the length of the azo group between the two sites increases. This surprising result is explained in terms of resonance effects and the larger electron-withdrawing power of longer azo linkers.



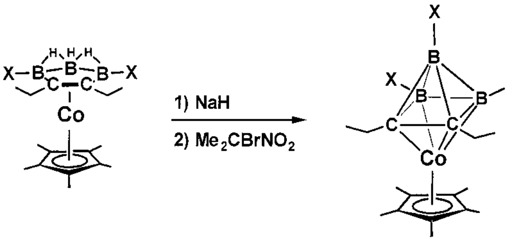
Angew. Chem. **2001**, *113*, 2775–2777

I. Chao,* T.-S. Hwang 2703–2705

Remote Communication between Charge Centers and Hydrogen-Bonding Sites: Possibility for a Signal Transducer?

Keywords: ab initio calculations · azo compounds · donor–acceptor systems · hydrogen bonds · through-bond interactions

Replacement of B–H hydrogen atoms with Cl or Br facilitates the previously unknown oxidative conversion of a *nido*- to a *closo*-6-vertex metallacarborane [Eq. (1); X = Cl, Br]. Oxidative cage closure, separation of carbon atoms upon thermal rearrangement, reductive cage opening, and cage expansion by boron insertion have all been applied to a single system, to afford synthetic access to new cluster types.



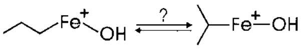
(1)

Angew. Chem. **2001**, *113*, 2777–2779

H.-J. Schanz, M. Sabat, R. N. Grimes* 2705–2707

nido ↔ *closo* Interconversion of Six-Vertex Metallacarboranes: Access to CoC_2B_3 and CoC_2B_4 Clusters with Nonadjacent Carbon Atoms

Keywords: boron • cage compounds • carboranes • cobalt • rearrangement



Transiently formed, constitutionally identical methyl groups remain inequivalent in the course of an *n*-propyl ⇄ isopropyl isomerization (see scheme) operative in Fe^+-mediated dehydration of propanols. The reversibility of the *β*-hydrogen transfer steps is addressed by examination of the H/D equilibration in metastable complexes of Fe^+ with a set of selectively deuterated propanols by using tandem mass spectrometry.

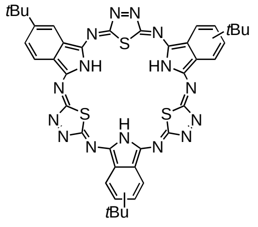
Angew. Chem. **2001**, *113*, 2780–2782

C. Trage, W. Zummack, D. Schröder, H. Schwarz* 2708–2710

Inherent Asymmetry of Constitutionally Equivalent Methyl Groups in the H/D Equilibration of *n*- and *i*-$C_3H_7Fe(OH)^+$ Complexes

Keywords: C–H activation • hydrogen transfer • iron • reaction mechanisms

Incorporation of three metal ions (Ni or Cu) in the macrocyclic ring and the formation of hexamers following a 3+3 approach are novel features of the hemiporphyrazines (one example shown) formed by the condensation of 2,5-diamino-1,3,4-triazole with isoindolediimines. This is in contrast to the corresponding reactions with diaminotriazoles, which afford 2+2 products.



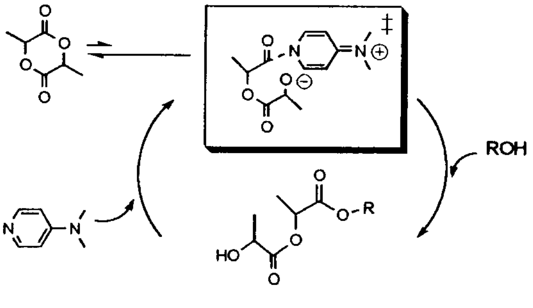
Angew. Chem. **2001**, *113*, 2782–2784

N. Kobayashi,* S. Inagaki, V. N. Nemykin, T. Nonomura 2710–2712

A Novel Hemiporphyrazine Comprising Three Isoindolediimine and Three Thiadiazole Units

Keywords: condensation reactions • heterocycles • macrocycles • phthalocyanines

A metal-free approach to the living ring-opening polymerization (ROP, shown schematically) of lactide has been developed using strongly basic amines such as 4-(dimethylamino)pyridine as transesterification catalysts. These organic catalysts must be used in combination with a nucleophile such as an alcohol, which is the actual initiating species.



Angew. Chem. **2001**, *113*, 2784–2787

F. Nederberg, E. F. Connor, M. Möller, T. Glauser, J. L. Hedrick* .. 2712–2715

New Paradigms for Organic Catalysts: The First Organocatalytic Living Polymerization

Keywords: catalysts • lactide • polymerization • ring-opening polymerization • transesterification

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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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