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INTERNATIONAL EDITION

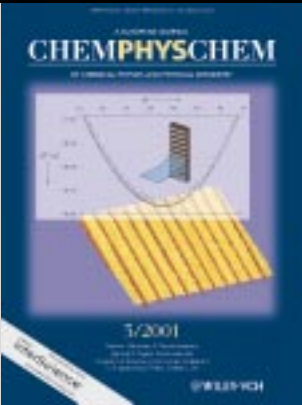
2001
40/6

Pages 969 – 1142



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*ChemPhysChem 3/2001 is bound
in this issue of Angewandte Chemie.*



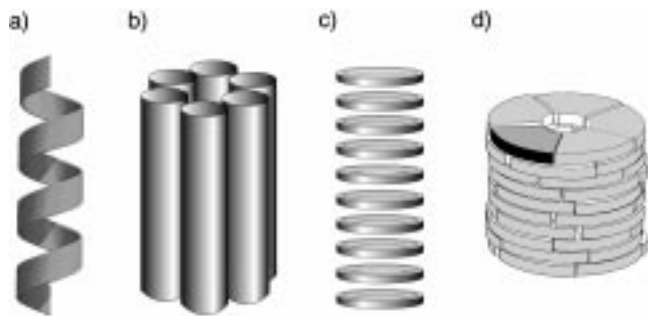
CHEMPHYSICHEM
A JOURNAL OF THE
DEUTSCHE CHEMISCHE GESELLSCHAFT
3/2001

COVER PICTURE

The cover picture shows an arrangement of ruthenium atoms representing the active site of ruthenium catalysts for ammonia synthesis. This B₅-type active site consists of three ruthenium atoms in one layer (blue spheres) and two ruthenium atoms in the layer directly above this (red spheres). This arrangement is energetically preferred, because none of the ruthenium atoms is in contact with both of the nitrogen atoms (green spheres) of the adsorbed N₂ molecule. Based on knowledge of this active site a number of catalysts were prepared by using [Ru₃(CO)₁₂] (upper green sphere) as a precursor. These catalysts were characterized (left red sphere and TEM micrograph in the background), tested using a parallel screening procedure (left and lower blue spheres), and kinetically analyzed (right blue sphere). The resulting barium-promoted Ru/MgO catalyst is the most active catalyst for ammonia synthesis to be described (right red sphere). It can be concluded that the B₅-type site also dominates the activity of the promoted catalysts (lower green sphere). The enormous catalytic potential of Ba-Ru/MgO is described by Muhler et al. on pp. 1061 ff.



Multiple strategies have been documented in recent years for the construction of tubular materials from self-organizing subunits. Cylindrical molecular compartments can be assembled by helical folding of linear species (a; see diagram), aggregation of rodlike molecules (b), stacking of molecular discs (c), or clustering of compounds with a truncated wedge-shape (d). Just as numerous are the applications of tubular materials; they are used as biosensors, novel antibiotics, biomaterials, molecular devices, and chemical catalysts.



Angew. Chem. **2001**, *113*, 1016–1041

D. T. Bong, T. D. Clark, J. R. Granja,
M. R. Ghadiri* 988–1011

Self-Assembling Organic Nanotubes

Keywords: crystal engineering •
materials science • nanotubes •
self-assembly • sensors

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>

Isolation and Structural Characterization of the Endohedral Fullerene $\text{Sc}_3\text{N@C}_{78}$

M. M. Olmstead,
A. de Bettencourt-Dias,
J. C. Duchamp, S. Stevenson,
D. Marciu, H. C. Dorn,*
A. L. Balch* ◆

Copper(I) Carbenes: The Synthesis of Active Intermediates in Copper-Catalyzed Cyclopropanation

B. F. Straub, P. Hofmann* ◆

Synthesis of Conformationally Locked Carbohydrates: A Skew-Boat Conformation of L-Iduronic Acid Governs the Antithrombotic Activity of Heparin

S. K. Das, J.-M. Mallet,
J. Esnault, P.-A. Driguez,
P. Duchaussoy, P. Sizun,
J.-P. Hèrault, J.-M. Herbert,
M. Petitou,* P. Sinaÿ*

The First Phosphine Oxide Ligand Precursors for Transition Metal Catalyzed Cross-Coupling Reactions: C–C, C–N, and C–S Bond Formation on Unactivated Aryl Chlorides

G. Y. Li*

Cyclic Dimers of Metalloporphyrins as Tunable Hosts for Fullerenes: A Remarkable Effect of Rhodium(III)

J.-Y. Zheng, K. Tashiro,
Y. Hirabayashi, K. Kinbara,
K. Saigo,* T. Aida,*
S. Sakamoto, K. Yamaguchi

Modular Pyridinyl Peptide Ligands in Asymmetric Catalysis: Enantioselective Synthesis of Quaternary Carbon Atoms Through Cu-Catalyzed Allylic Substitutions

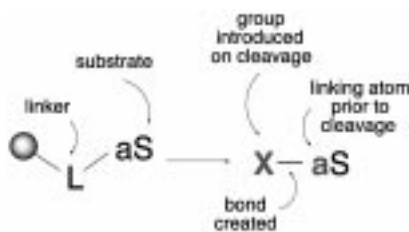
C. A. Luchaco-Cullis,
H. Mizutani, K. E. Murphy,
A. H. Hoveyda*

Direct Observation of Surface-Controlled Self-Assembly of Coordination Cages by using Atomic Force Microscopy as a Molecular Ruler

S. A. Levi, P. Guatterì,
F. C. J. M. van Veggel,
G. J. Vancso, E. Dalcanele,
D. N. Reinhoudt*

What is “tracelessness” really? The term refers to solid-phase organic synthesis in which the cleaved product contains no vestige of the linker; at least three quite distinct definitions are in current use. Nomenclature is essential for the efficient communication of ideas and a more rigid and comprehensible terminology (see scheme) will clear the mists from a rather cloudy aspect of this very important field.

Angew. Chem. **2001**, *113*, 1042–1063



A. C. Comely,*
S. E. Gibson (née Thomas) .. 1012–1032

Tracelessness Unmasked: A General Linker Nomenclature

Keywords: combinatorial chemistry • solid-phase synthesis • traceless linkers

ESSAY

Struggling with nature is certainly a familiar feeling to many of us. This particular metaphor began life, however, after another wrestling bout, in a striking classical allusion by Francis Bacon in 1605. We trace the evolution of the metaphor through the centuries and the way it has been invoked in opposition to science. Is it possible to experiment without intrusion?

Angew. Chem. **2001**, *113*, 1065–1068

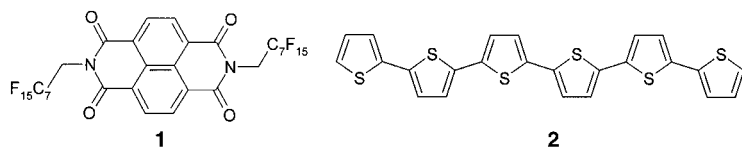
R. Hoffmann,*
P. Laszlo* 1033–1036

Protean

Keywords: history of chemistry • history of science

HIGHLIGHTS

Comparatively simple organic compounds such as naphthalenebisimides (**1**) and oligothiophenes (**2**) could become mass products in future flexible electronic devices. Several research groups have already made significant advances towards this. The next challenge to be mastered is the controlled deposition of substances from solution.



Angew. Chem. **2001**, *113*, 1069–1071

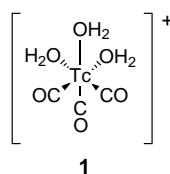
F. Würthner* 1037–1039

Plastic Transistors Reach Maturity for Mass Applications in Microelectronics

Keywords: conducting materials • microelectronics • naphthaleneimides • oligothiophenes • semiconductors

You believe that organometallic compounds are sensitive towards air and moisture and can only be handled under an inert atmosphere? Wrong! Recent work by several groups shows how organometallic compounds, such as the Tc compound **1**, are successfully used for the detection of biomolecules in an aerobic, aqueous environment. Using **1**, the radiolabeling of single-chain antibody fragments and serotonergic receptors in the central nervous system has been possible for the first time.

Angew. Chem. **2001**, *113*, 1072–1076

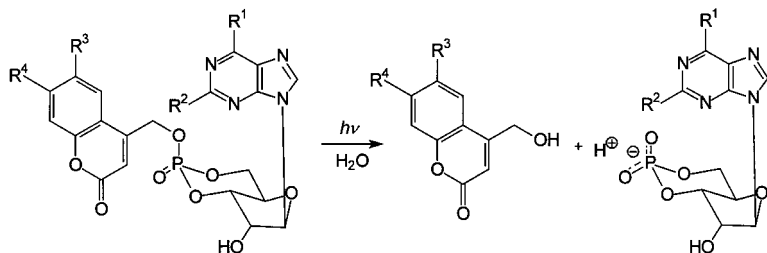


N. Metzler-Nolte* 1040–1043

Labeling of Biomolecules for Medicinal Applications—Bioorganometallic Chemistry at Its Best

Keywords: bioinorganic chemistry • bioorganometallic chemistry • biosensors • medicinal chemistry • ruthenium • technetium

Caged cyclic nucleotides exhibiting remarkable advantageous properties have been developed through the use of novel photolabile coumarinylmethyl protecting groups (see scheme). They serve as excellent intracellular sources of cAMP and cGMP and allow the study of spatial- and time-dependent aspects of cyclic nucleotide signaling.



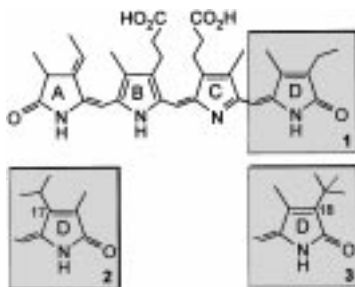
Angew. Chem. **2001**, *113*, 1078–1080

V. Hagen,* J. Bendig, S. Frings,
T. Eckardt, S. Helm, D. Reuter,
U. B. Kaupp 1046–1048

Highly Efficient and Ultrafast
Phototriggers for cAMP and cGMP by
Using Long-Wavelength UV/Vis-
Activation

Keywords: ion channels • nucleotides •
photolysis • protecting groups • signal
transduction

The assembly kinetics of open-chain tetrapyrroles in a recombinant apo-phytochrome and the thermal reversal of the P_{fr} to the P_r form of the phytochrome are strongly affected by steric interactions between the protein and the chromophore. Relative to the chromoprotein with a naturally occurring chromophore (**1**), bulkier alkyl groups on ring D regioselectively retard the incorporation and covalent binding (whereby C17 derivatives, particularly the 17- $\text{CH}(\text{CH}_3)_2$ derivative **2**, have a larger effect than C18 derivatives), and either decrease or increase the thermal stability of the P_{fr} form with increasing substituent size at C17/C18, respectively (the 18- $\text{C}(\text{CH}_3)_3$ derivative **3** shows the largest effect here).



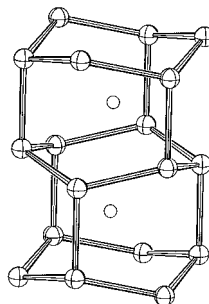
Angew. Chem. **2001**, *113*, 1080–1082

U. Robben, I. Lindner, W. Gärtner,*
K. Schaffner 1048–1050

Analysis of the Topology of the
Chromophore Binding Pocket of
Phytochromes by Variation of the
Chromophore Substitution Pattern

Keywords: chromophores •
isomerization • kinetics •
photochromism • phytochromism •
tetrapyrroles

At 4 GPa and 900°C, hexagonal high-pressure LiGe—a Zintl phase—with a new structural motif was prepared: isolated hexagonal channels built up by three-coordinate Ge^- ions. These channels consist of puckered germanium six-membered rings of distorted chairs and boats (see picture). Li^+ counterions are found in the centers of the channels and in the symmetry-equivalent positions between the channels.



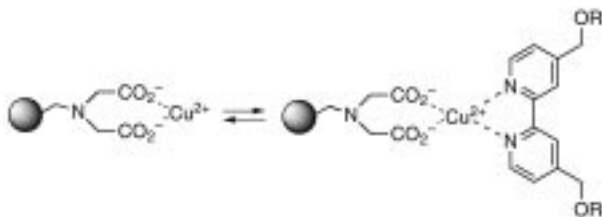
Angew. Chem. **2001**, *113*, 1085–1088

J. Evers,* G. Oehlinger 1050–1053

Isolated Hexagonal Channels Built up by
Three-Connected Ge^- Ions in LiGe at
High Pressure

Keywords: germanium • high-pressure
chemistry • lithium • structure
elucidation • Zintl phases

Simple purification of compounds can be achieved using a bipyridine unit as a tag and resin-bound metal ions. The usefulness of this method (see scheme) is demonstrated by the multistep synthesis of a small library of hydantoin and benzodiazepines.



Angew. Chem. **2001**, *113*, 1088–1090

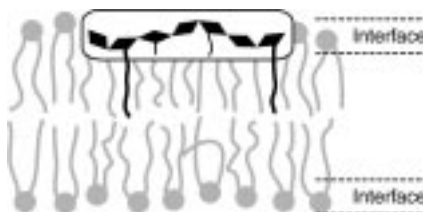
S. V. Ley,* A. Massi, F. Rodríguez,
D. C. Horwell, R. A. Lewthwaite,
M. C. Pritchard,*
A. M. Reid 1053–1055

A New Phase-Switch Method for
Application in Organic Synthesis
Programs Employing Immobilization
through Metal-Chelated Tagging

Keywords: chelates • combinatorial
chemistry • immobilization • N ligands •
separation methods

A double lipid-modified peptide

which mimics the seven amino acids of the C terminus of the N-Ras protein has been investigated by high-resolution ^1H magic angle spinning NMR spectroscopy. The axially symmetric motion of the peptide in the bilayer decreases the NMR line widths, which facilitates signal assignment and localization of the peptide in the membrane. The peptide is located in the lipid/water interface of the lipid membrane (see schematic representation).



Angew. Chem. **2001**, *113*, 1083–1085

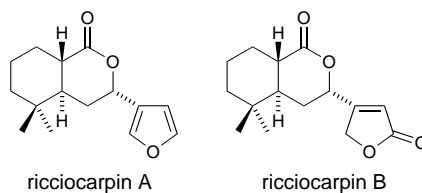
D. Huster, K. Kuhn, D. Kadereit,
H. Waldmann, K. Arnold* .. 1056–1058

^1H High-Resolution Magic Angle
Spinning NMR Spectroscopy for the
Investigation of a Ras Lipopeptide in a
Lipid Membrane

Keywords: lipids • membranes •
NMR spectroscopy • peptides

The furanosesquiterpene lactone

ricciocarpin A isolated from a liverwort displays high molluscicidal activity. By twofold application of the catalytic ring-closing metathesis a fast access to the enantiomerically pure title compounds was achieved, and their absolute configuration determined.



ricciocarpin A

ricciocarpin B

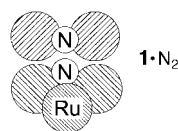
Angew. Chem. **2001**, *113*, 1091–1093

C. Held, R. Fröhlich,
P. Metz* 1058–1060

Enantioselective Synthesis of the
Ricciocarpins A and B

Keywords: metathesis • natural products •
sesquiterpenes • structure elucidation •
total synthesis

A high potential to save energy in the production of ammonia is possible with the ruthenium catalysts developed by a knowledge-based approach using a parallel screening procedure. The high activity of these catalysts is dominated by the B₅-type site **1**.



H. Bielawa, O. Hinrichsen, A. Birkner,
M. Muhler* 1061–1063

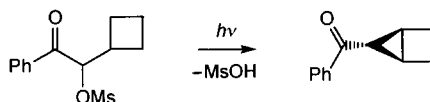
The Ammonia-Synthesis Catalyst of the
Next Generation: Barium-Promoted
Oxide-Supported Ruthenium

Keywords: ammonia synthesis •
heterogeneous catalysis • ruthenium •
screening methods

Angew. Chem. **2001**, *113*, 1093–1096

Especially highly substituted cyclopropanes

can be produced with a new photochemical approach. Starting with aromatic ketones that bear a leaving group adjacent to the carbonyl carbon atom, photolysis leads to the formation of 1,3-diradicals, which efficiently cyclize to cyclopropanes (see scheme; Ms = MeSO₂).



P. Wessig,* O. Mühling 1064–1065

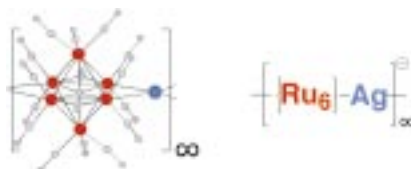
A New Photochemical Route to
Cyclopropanes

Keywords: bicycles • cyclopropanes •
diradicals • Norrish–Yang reaction •
photochemistry

Angew. Chem. **2001**, *113*, 1099–1101

Surprisingly stable

are the first cluster-containing molecular wires prepared by self-assembly of hexaruthenium cluster anions with silver cations. X-ray characterization reveals a unique structure with infinite, heteroleptic metal–metal bonded anionic chains (see picture) that are isolated by layers of counterions.



T. Nakajima, A. Ishiguro,
Y. Wakatsuki* 1066–1068

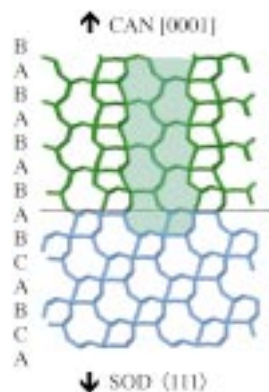
Formation of Super Wires of Clusters by
Self-Assembly of Transition Metal Cluster
Anions with Metal Cations

Keywords: cluster compounds •
coordination polymer • ruthenium • self-
assembly • silver

Angew. Chem. **2001**, *113*, 1096–1099

Parallel hexagonal prisms of cancrinite (CAN) with channels perpendicular to the substrate surface were obtained by heteroepitaxial growth on millimeter-sized sodalite (SOD) single crystals. The experiment was planned on the basis of a model in which the ABABAB stacking sequences along the cancrinite [0001] direction were connected to the ABCABC sequence along the sodalite $\langle 111 \rangle$ direction (see schematic diagram).

Angew. Chem. **2001**, *113*, 1103–1105



T. Okubo,* T. Wakiyama, J. Plévert,
S. Nair, M. Tsapatsis, Y. Ogawa,
H. Komiyama, M. Yoshimura,
M. E. Davis 1069–1071

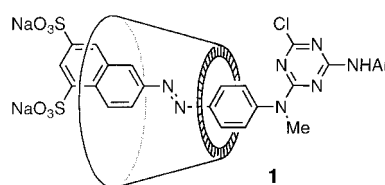
Heteroepitaxial Growth of a Zeolite

Keywords: crystal growth • microporosity
• zeolites



A “cyclodextrin coat” dramatically enhances the stability of an azo dye towards reductive bleaching, oxidative bleaching, and photo-bleaching as is demonstrated by the rotaxane **1**. This compound is obtained as a single isomer in high yield from the amine-substituted dye and trichlorotriazine in water in the presence of the cyclodextrin.

Angew. Chem. **2001**, *113*, 1105–1108



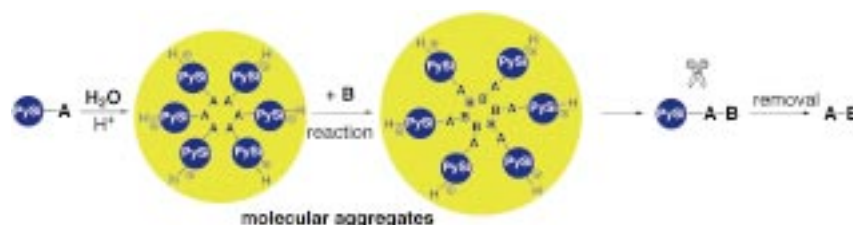
M. R. Craig, M. G. Hutchings,
T. D. W. Claridge,
H. L. Anderson* 1071–1074

Rotaxane-Encapsulation Enhances the
Stability of an Azo Dye, in Solution and
when Bonded to Cellulose

Keywords: azo compounds •
cyclodextrins • dyes/pigments •
rotaxanes • supramolecular chemistry



Dramatic rate enhancements are observed in aqueous Diels–Alder reactions between 1,3-dienes substituted with 2-pyridyldimethylsilyl (PySi) groups and *p*-benzoquinone in the presence of HCl. The hydrophilic PySi group induces molecular aggregation in water, thus enabling organic reactions to occur at hydrophobic reaction sites located within the aggregates (see scheme).



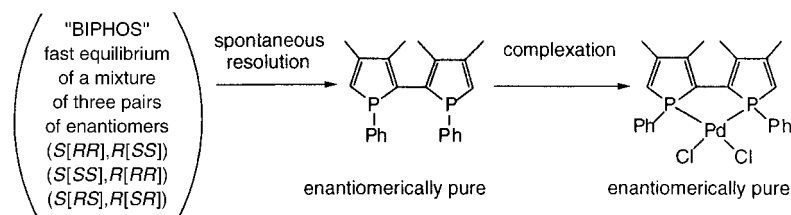
Angew. Chem. **2001**, *113*, 1108–1110

K. Itami, T. Nokami,
J.-i. Yoshida* 1074–1076

2-Pyridyldimethylsilyl as a Removable
Hydrophilic Group in Aqueous Diels–
Alder Reactions

Keywords: aggregation • cycloaddition •
silicon • solvent effects • surfactants

Enantiomerically pure BIPHOS was obtained by spontaneous resolution through the crystallization of a racemic mixture, without the use of chemical or physical chiral auxiliaries, and was used in the synthesis of the enantiomerically pure complex $[\text{PdCl}_2(\text{biphos})]$ (see scheme). The complex proved to be efficient in catalytic asymmetric allylic substitutions with 80% *ee*.



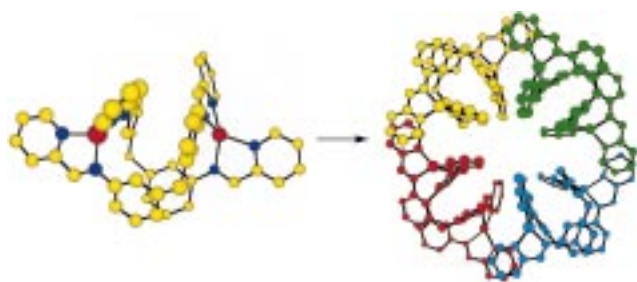
Angew. Chem. **2001**, *113*, 1110–1112

O. Tissot, M. Gouygou,*
F. Dallemer, J.-C. Daran,
G. G. A. Balavoine* 1076–1078

The Combination of Spontaneous
Resolution and Asymmetric Catalysis:
A Model for the Generation of Optical
Activity from a Fully Racemic System

Keywords: allylation • asymmetric
catalysis • P ligands • palladium •
spontaneous resolution

Arc-shaped helicate units are readily prepared from simple pyridylimine ligands. The arc-shaped topography controls their aggregation and a four-unit circular array of 2.5 nm diameter results (see scheme).



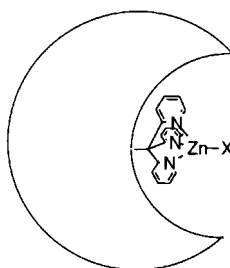
Angew. Chem. **2001**, *113*, 1113–1115

L. J. Childs, N. W. Alcock,
M. J. Hannon* 1079–1081

Assembly of Nano-Scale Circular
Supramolecular Arrays Through π – π
Aggregation of Arc-Shaped Helicate
Units

Keywords: helical structures • N ligands •
nanostructures • self-assembly •
supramolecular chemistry

Incorporation of a tripodal N_3 -donor ligand at the base of a designed molecular cleft generated inside a high molecular weight dendritic structure (see picture) allows the coordination behavior of the ligand to be controlled. This approach, using designed dendrimer clefts, has the potential to be extended to a range of different coordination environments.



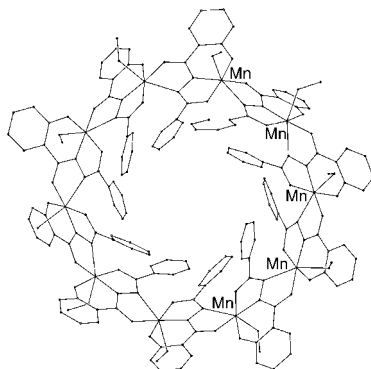
Angew. Chem. **2001**, *113*, 1115–1118

M. J. Hannon,* P. C. Mayers,
P. C. Taylor* 1081–1084

A Dendritic Structure Containing a
Designed Cleft which Controls Ligand
Coordination Behavior in an Analogous
Way to Proteins

Keywords: biomimetic chemistry •
coordination chemistry • dendrimers •
N ligands • zinc

A planar decanuclear 30-membered core ring is present in the new manganese (see picture) and iron [30]azametallacrown-10 compounds. These compounds were prepared by using the pentadentate ligand *N*-phenylsalicylhydrazide, and the metal atoms in each ring adopt a propeller configuration and have alternating Δ/Λ stereochemistries.



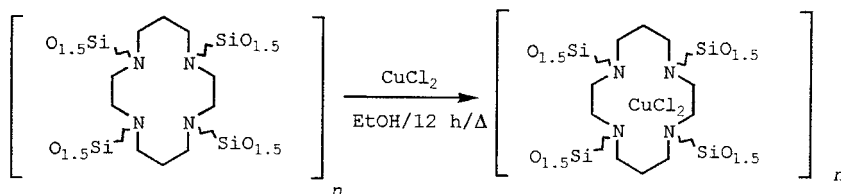
Angew. Chem. **2001**, *113*, 1118–1121

S.-X. Liu,* S. Lin, B.-Z. Lin, C.-C. Lin,
J.-Q. Huang 1084–1087

[30]Metallacrown-10 Compounds:
[Mn(C₁₄H₉N₂O₃)(CH₃OH)]₁₀ · 5 CH₂Cl₂ ·
16 CH₃OH · H₂O and
[Fe(C₁₄H₉N₂O₃)(CH₃OH)]₁₀ · 3 CH₂Cl₂ ·
12.5 CH₃OH · 5 H₂O

Keywords: crown compounds • iron •
manganese • metallacrown compounds •
supramolecular chemistry

Two routes, two materials: metal salts are incorporated into cyclam-containing hybrid materials either by the polycondensation of metal salt/silylated-cyclam complexes or by the direct incorporation of metal salts into the xerogels (see scheme). These routes are not equivalent, only the latter gives products showing metal–metal interactions. This result suggests a new coordination chemistry within nanostructured hybrid materials.



Angew. Chem. **2001**, *113*, 1121–1124

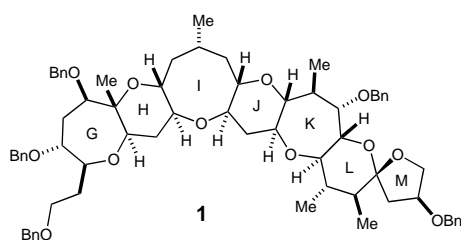
G. Dubois, C. Reyé, R. J. P. Corriu,*
S. Brandès, F. Denat,
R. Guillard* 1087–1090

Coordination Chemistry in the Solid:
Study of the Incorporation of Cu^{II} into
Cyclam-Containing Hybrid Materials

Keywords: copper • EPR spectroscopy •
macrocycles • metal–metal interactions •
sol–gel process



Access to polycyclic polyethers is facilitated by a synthetic strategy involving two-step *B*-alkyl Suzuki coupling reactions for the stereo-selective construction of the poly-ether skeleton. Thus, a convergent synthetic route to the heptacyclic GHIJKLM ring system **1** of ciguatoxin, a marine algal toxin implicated in ciguatera fish poisoning, was developed. Bn = benzyl.



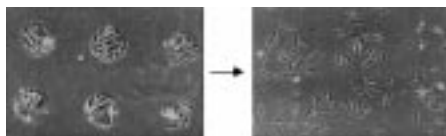
H. Takakura, K. Noguchi, M. Sasaki,*
K. Tachibana 1090–1093

Synthetic Studies on Ciguatoxin:
A Highly Convergent Synthesis of the
GHIJKLM Ring System Based on
B-Alkyl Suzuki Coupling

Keywords: ciguatoxin • cross-coupling •
natural products • polycycles • synthetic
methods

Angew. Chem. **2001**, *113*, 1124–1127

A dynamic surface can “turn on” the migration of adherent cells. This dynamic property is based on a self-assembled monolayer that presents hydroquinone groups. Electrochemical oxidation converts the hydroquinone into the corresponding benzoquinone, which then undergoes a Diels–Alder reaction with a conjugate of cyclopentadiene and a peptide ligand. This in situ modification of the substrate gives a surface that promotes cell migration (see scheme).



M. N. Yousaf, B. T. Houseman,
M. Mrksich* 1093–1096

Turning On Cell Migration with
Electroactive Substrates

Keywords: bioorganic chemistry • cell
migration • Diels–Alder reaction •
monolayers • oxidation

Angew. Chem. **2001**, *113*, 1127–1130



Helicenes without any heteroatoms have been shown for the first time to act as chiral inducers in the highly enantioselective addition of diisopropylzinc to an aldehyde (see scheme).



I. Sato, R. Yamashima, K. Kadowaki,
J. Yamamoto, T. Shibata,
K. Soai* 1096–1098

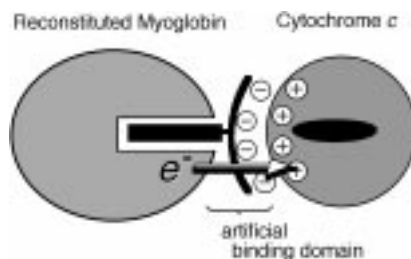
Asymmetric Induction by Helical
Hydrocarbons: [6]- and [5]Helicenes

Keywords: asymmetric amplification •
asymmetric catalysis • autocatalysis •
chirality • helical structures

Angew. Chem. **2001**, *113*, 1130–1132



Protein–protein recognition at a molecular level was investigated and its importance in interprotein electron transfer (ET) assessed by using novel synthetic models. The binding properties and overall ET reaction processes (see scheme) were controlled by the interfacial dynamics within the reconstituted myoglobin–cytochrome *c* complex.



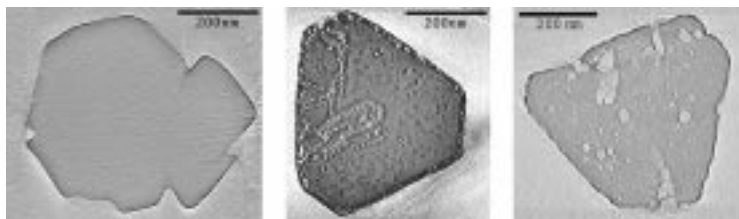
Y. Hitomi, T. Hayashi,* K. Wada,
T. Mizutani, Y. Hisaeda,
H. Ogoshi 1098–1101

Interprotein Electron Transfer Reaction
Regulated by an Artificial Interface

Keywords: electron transfer • heme
proteins • myoglobin • protein–protein
recognition • zinc

Angew. Chem. **2001**, *113*, 1132–1135

Mesopore formation in zeolite Y upon hydrothermal treatment results in cavities inside the zeolite crystals rather than cylindrical pores that connect the external surface to the interior of the crystal. This conclusion follows from the three-dimensional visualization of the mesopores. The three images below show the development of these micropores upon extended hydrothermal treatment.



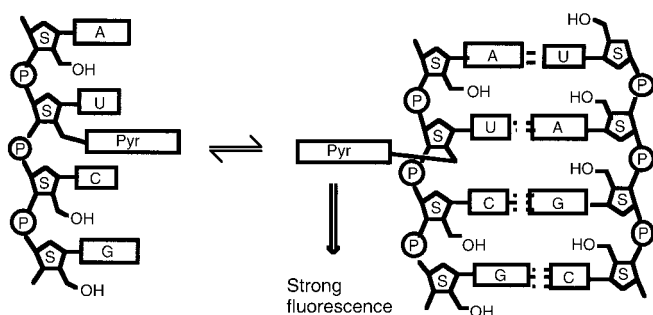
Angew. Chem. **2001**, *113*, 1136–1138

A. H. Janssen, A. J. Koster,
K. P. de Jong* 1102–1104

Three-Dimensional Transmission
Electron Microscopic Observations of
Mesopores in Dealuminated Zeolite Y

Keywords: catalysts • electron
microscopy • mesoporosity • zeolites

Labeling the 2'-hydroxy function of RNA with a pyrenylmethyl group (Pyr) provides a useful probe of RNA because of its high fluorescent quantum efficiency on binding. The fluorescence exhibits sequence specificity and binds with a high affinity (see schematic representation).



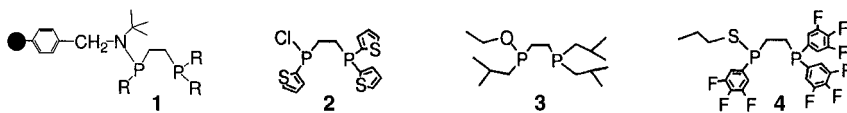
Angew. Chem. **2001**, *113*, 1138–1140

K. Yamana,* H. Zako, K. Asazuma,
R. Iwase, H. Nakano,
A. Murakami 1104–1106

Fluorescence Detection of Specific RNA
Sequences Using 2'-Pyrene Modified
Oligoribonucleotides

Keywords: fluorescence •
oligonucleotides • RNA recognition

A simple route to new diphosphane ligands: Merrifield's resin was used to construct diphosphanes of the general formula **1** that could be cleaved by reaction with PCl_3 , alcohols, or thioalcohols to provide ligands such as **2–4** in solution.



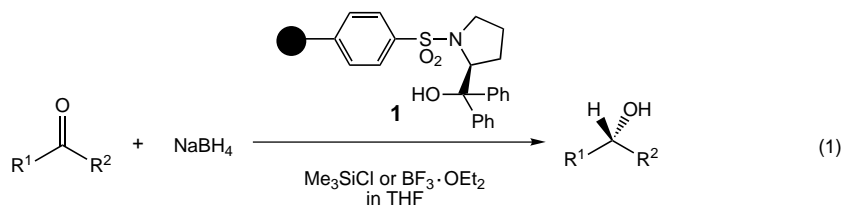
Angew. Chem. **2001**, *113*, 1140–1143

G. Y. Li,* P. J. Fagan,
P. L. Watson 1106–1109

Versatile Approaches to the Polymer-
Supported Synthesis of Bidentate
Phosphorus-Containing Ligands

Keywords: combinatorial chemistry •
homogeneous catalysis • P ligands •
phosphanes • solid-phase synthesis

Two remarkable reducing agents $\text{NaBH}_4/\text{Me}_3\text{SiCl}$ (or $\text{BF}_3 \cdot \text{OEt}_2$) in combination with a new kind of chiral, polymer-supported *N*-sulfonamide catalyst **1** were applied to the reduction of prochiral ketones giving excellent chemical yields and enantiomeric excesses [Eq. (1)].



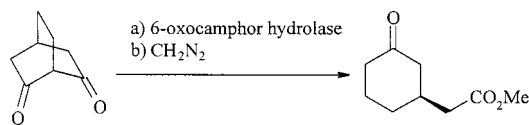
Angew. Chem. **2001**, *113*, 1143–1145

J.-b. Hu, G. Zhao,*
Z.-d. Ding 1109–1111

Enantioselective Reduction of Ketones
Catalyzed by Polymer-Supported
Sulfonamide Using $\text{NaBH}_4/\text{Me}_3\text{SiCl}$
(or $\text{BF}_3 \cdot \text{OEt}_2$) as Reducing Agent

Keywords: asymmetric synthesis •
heterogeneous catalysis • reductions •
sulfonamides

Unsymmetrical is beautiful: Enzymatic desymmetrization offers a mild route to chiral synthons with, in principle, 100% yield and absolute optical purity. The technique has been applied to bicyclic β -diketones for the first time, through a novel enzymatic retro-Claisen reaction, to yield chiral cyclic keto acids in up to 91% yield and 94% *ee* (see scheme, step a).




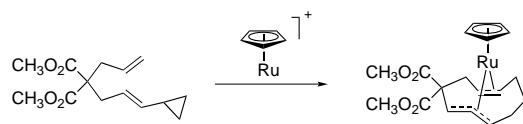
Angew. Chem. **2001**, *113*, 1145–1148

G. Grogan,* J. Graf, A. Jones, S. Parsons, N. J. Turner,* S. L. Flitsch* . 1111–1114

An Asymmetric Enzyme-Catalyzed Retro-Claisen Reaction for the Desymmetrization of Cyclic β -Diketones

Keywords: biotransformations • enzyme catalysis • hydrolases • hydrolysis

 **The reaction of coordinatively unsaturated ruthenium(II)** with a tethered (alkenylvinyl)cyclopropane results in the preparation of the first (cyclodecadienyl)ruthenium complex (see scheme; open coordination sites on the ruthenium center may be occupied by the solvent (acetone) or acetonitrile). This unprecedented reaction raises intriguing mechanistic and synthetic possibilities.



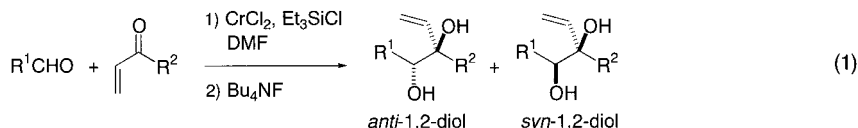
Angew. Chem. **2001**, *113*, 1148–1150

B. M. Trost,* F. D. Toste ... 1114–1116

Synthesis of the First (1-3:6,7- η -Cyclodecadienyl)ruthenium Complex by the Intramolecular Reaction of an Alkene and a Vinylcyclopropane

Keywords: allyl complexes • C–H activation • cycloisomerization • ruthenium • vinylcyclopropanes

Efficient trapping of chromium enolates in the presence of Et_3SiCl gives silyl enol ethers. This trapping changes the course of the reaction between α,β -unsaturated ketones and aldehydes from a sequential aldol–cyclopropanol formation to a cross pinacol-type coupling reaction [Eq. (1); for example, $\text{R}^1 = n\text{-C}_8\text{H}_{17}$, $\text{R}^2 = \text{Ph}(\text{CH}_2)_2$]. The *anti/syn* ratios of the 1,2-diols depend on the reaction temperature.



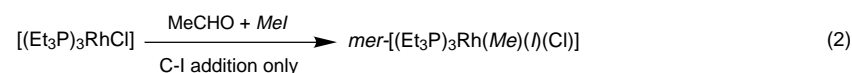
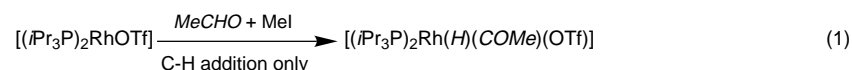
Angew. Chem. **2001**, *113*, 1150–1153

K. Takai,* R. Morita, C. Toratsu 1116–1119

Stereoselective Cross Pinacol-Type Coupling between α,β -Unsaturated Ketones and Aldehydes Mediated by Chromium(II) and R_3SiCl

Keywords: aldehydes • chromium • diols • ketones • pinacol coupling

The strikingly different reactivity of similar complexes of the type $[\text{P}_n\text{RhX}]$ is strongly dependent on the number and nature of the trialkylphosphane (P) and of the anionic ligand (X), and can be selectively directed to the oxidative addition of either aldehydes or MeI [Eqs. (1) and (2)].



Angew. Chem. **2001**, *113*, 1153–1156

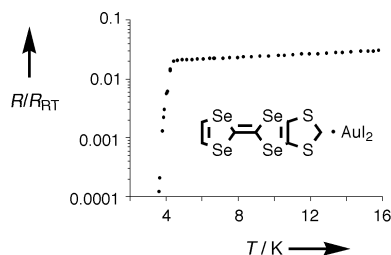
R. Goikhman, D. Milstein* 1119–1122

Ligand-Controlled Chemoselectivity in the Classical Oxidative Addition Reactions of MeI and Aldehydes to Rhodium(I) Complexes

Keywords: aldehydes • chemoselectivity • oxidative addition • rhodium



The radical cationic salt of methylenedithiotetraselenafulvalene (MDT-TSF), shown in the picture, was formed on its treatment with AuI_2^- . The salt showed a superconducting transition at 4.5 K (onset) at ambient pressure. The crystal structure of the MDT-TSF cation is completely planar and stacked along its *a*-axis; the calculated overlap integral is five times greater in the intrastack compared to the interstack direction and the material is therefore quasi one-dimensional.



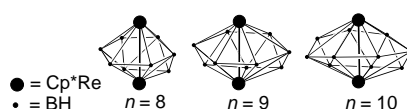
K. Takimiya,* Y. Kataoka, Y. Aso,
T. Otsubo,* H. Fukuoka,
S. Yamanaka 1122–1125

Quasi One-Dimensional Organic
Superconductor MDT-TSF·AuI₂ with
T_c = 4.5 K at Ambient Pressure

Keywords: conducting materials • radical ions • selenium • superconductors

Angew. Chem. **2001**, *113*, 1156–1159

Different cluster–structure electron-counting rules to those of either boranes or metallaboranes of later transition metals are obeyed by the metallaboranes formed from the earlier transition metals. This principle is confirmed by the existence and structures of the homologous series of rhenaboranes $[(\text{Cp}^*\text{Re})_2\text{B}_n\text{H}_n]$, $n = 7–10$ (see scheme).



S. Ghosh, M. Shang, Y. Li,
T. P. Fehlner* 1125–1128

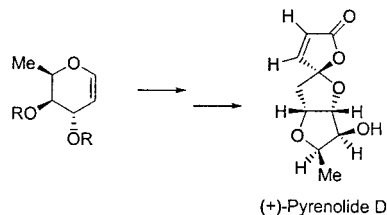
Synthesis of $[(\text{Cp}^*\text{Re})_2\text{B}_n\text{H}_n]$ $n = 8–10$:
Metal Boride Particles that Stretch the
Cluster Structure Paradigms

Keywords: boron • carboranes • cluster compounds • rhenium

Angew. Chem. **2001**, *113*, 1159–1162



The direct stereoselective I^{III}-mediated oxidative ring contraction of a protected 6-deoxy-D-gulal substrate to form a highly functionalized tetrahydrofurfural intermediate is a key step in the first total synthesis of (+)-pyrenolide D (see scheme; R = TBS = *tert*-butyldimethylsilyl).



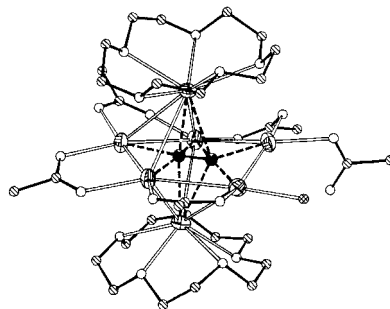
K. M. Engstrom, M. R. Mendoza,
M. Navarro-Villalobos,
D. Y. Gin* 1128–1130

Total Synthesis of (+)-Pyrenolide D

Keywords: glycals • hypervalent compounds • pyrenolide • ring contractions • total synthesis

Angew. Chem. **2001**, *113*, 1162–1164

Silver double salts containing embedded C_2^{2-} ions have been isolated by using [15]crown-5 (15C5) as a structure-directing agent. Unprecedented low dimensionalities are found for these compounds, which exist either as discrete molecules or as a zigzag chain. They feature different kinds of silver cages each sandwiched by a pair of η^5 -15C5 ligands: pentagonal bipyramidal $\text{C}_2@Ag_7$ (see picture) and $(\text{C}_2)_2@Ag_{13}$ double cage (two square antiprisms sharing a common triangular face).



Q.-M. Wang, T. C. W. Mak* . 1130–1133

Crown-Ether-Directed Assembly of
Discrete and One-Dimensional Silver
Aggregates Containing Embedded
Acetylenediide

Keywords: argentophilicity • carboxylato complexes • cluster compounds • crown compounds • silver

Angew. Chem. **2001**, *113*, 1164–1167



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* Author to whom correspondence should be addressed



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<http://www.angewandte.com>

CORRIGENDA

In the Communication by **S. Bobev** and **S. C. Sevov** in Issue 22, 2000, pp. 4108–4110 the references to the discovery (J. D. Corbett, *Inorg. Nucl. Chem. Lett.* **1967**, 3, 173 and *Inorg. Chem.* **1968**, 7, 1980) and the early characterization of Bi_8^{2+} (B. Krebs et al., *Angew. Chem.* **1982**, 94, 453; *Angew. Chem. Int. Ed. Engl.* **1982**, 21, 445 as well as *Chem. Ber.* **1996**, 129, 1219) were omitted. Bi_8^{2+} , which is isoelectronic and isostructural to Sn_8^{6-} , is also the first square-antiprismatic cluster of eight atoms.

In the Communication by **G. Siuzdak** and **W. H. Benner** et al. in Issue 3, 2001, pp. 541–544 the following information was omitted: The first direct mass measurement of a virus was made with TMV ions using the instrument invented at Berkeley (Fuerstenau et al., US Patent 5770857). Those experiments were reported by Fuerstenau and Benner in a poster entitled “Weighing Intact Virus Particles with a Charge Detection Mass Spectrometer” presented at the “44th ASMS Conference on Mass Spectrometry and Allied Topics, Portland, USA, 1996). Some time later, Siuzdak and co-workers visited Berkeley and obtained the results on the RYMV virus using this same instrument.

The correct ISBN of the Book “Chemistry of Fireworks” by M. S. Russell reviewed in Issue 1, 2001, p. 259 is 0-85404-598-8.