

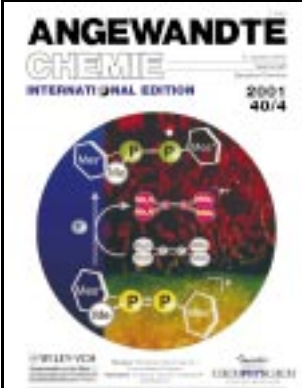
ANGEWANDTE CHEMIE

A Journal of the
Gesellschaft
Deutscher Chemiker

INTERNATIONAL EDITION

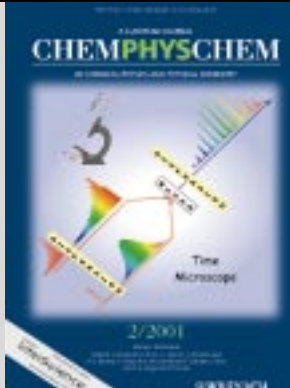
**2001
40/4**

Pages 635–804



**ANGEWANDTE
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INTERNATIONAL EDITION
2001
40/4

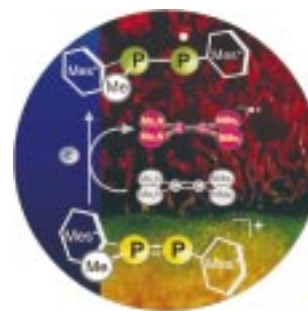
ChemPhysChem 2/2001 is bound
in this issue of *Angewandte Chemie*.



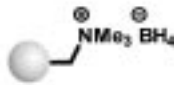
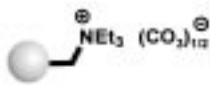
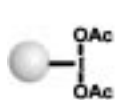
CHEMPHYSCHEM
A JOURNAL OF PHYSICAL CHEMISTRY
2/2001
WILEY-VCH

COVER PICTURE

The cover picture shows the array of colors observed in the synthesis of the long-lived phosphorus radicals $[\text{Mes}^*\text{MeP}=\text{PMes}^*]^{\bullet}$ (**3**; $\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_3$). These colors were obtained by layering a colorless solution of the electron-rich tetrakis(dimethylamino)ethylene (**2**) in acetonitrile onto a yellow solution of the phosphonium salt $[\text{Mes}^*\text{MeP}=\text{PMes}^*]^+[\text{O}_3\text{SCF}_3]^-$ (**1**) in acetonitrile. An immediate intense green color characteristic of solute **3** formed at the phase boundary. At the same time orange-red crystals of **3** appeared and deposited on the walls of the container. The red color denotes the formation of the radical cation $[(\text{Me}_2\text{N})_3\text{C}_2]^{\bullet+}$. More about this reaction, which has allowed the first isolation of diphosphanyl radicals, is described by Geoffroy, Grützmacher, and co-workers on page 723 ff.



A bright future for automated synthesis in solution: Functionalized polymers (see picture) have emerged as versatile synthetic tools for transforming reactants or removing by-products and impurities from solution, and have been employed successfully in multistep syntheses without the need for any further purification steps.



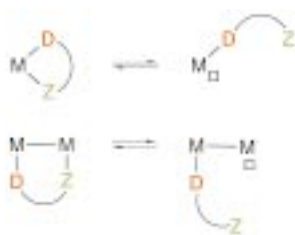
Angew. Chem. **2001**, *113*, 670–701

A. Kirschning,* H. Monenschein,
R. Wittenberg 650–679

Functionalized Polymers—Emerging
Versatile Tools for Solution-Phase
Chemistry and Automated Parallel
Synthesis

Keywords: automated synthesis •
combinatorial chemistry • functionalized
polymers • reagents

Ligand design—an essential part of synthetic chemistry! Ligands with different chemical functions (D and Z), such as hard and soft donors, are known as hybrid ligands. Such ligands can have hemilabile properties (see scheme) and find increasing use for tailoring the properties of metal complexes and designing new systems for molecular activation, homogeneous catalysis, functional materials, and small-molecule sensing. This review concentrates on multifunctional ligands with oxazoline moieties for which hemilabile properties were unknown until very recently.



Angew. Chem. **2001**, *113*, 702–722

P. Braunstein,* F. Naud * 680–699

Hemilability of Hybrid Ligands
and the Coordination Chemistry of
Oxazoline-Based Systems

Keywords: coordination chemistry •
homogeneous catalysis • hybrid ligands •
ligand design • 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>

From Oligomers to Conducting Polymers of the Metal–Dinitrogen
Functionality

Heterogeneous Dinuclear Rhodium(II) Hydroformylation Catalysts—Per-
formance Evaluation and Silsesquioxane-Based Chemical Modeling

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

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

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

Isolation and Structural Characterization of the Endohedral Fullerene
Sc₃N@C₇₈

E. Solari, J. Hesschenbrouck, ◆
R. Scopelliti, C. Floriani,* N. Re

M. Nowotny,* T. Maschmeyer, ◆
B. F. G. Johnson, P. Lahuerta,
J. M. Thomas, J. E. Davies

T. Nakajima, A. Ishiguro,
Y. Wakatsuki*

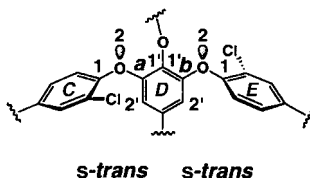
S. K. Das, J.-M. Mallet,
J. Esnault, P.-A. Driguez,
P. Duchaussoy, P. Sizun,
J.-P. Hèrault, J.-M. Herbert,
M. Petitou,* P. Sinaï*

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

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

Great confusion is often caused by the description of the configuration of molecules with numerous stereoelements, for example, complex natural products, with the CIP system. An example is given here (see picture), that of vancomycin, a glycopeptide antibiotic, whose different stereogenic units are described and a convention for the unambiguous notation for the stereogenic axes is proposed that is hoped will clarify future scientific publications.

Angew. Chem. **2001**, *113*, 723–726



K. C. Nicolaou,* C. N. C. Boddy,
J. S. Siegel* 701–704

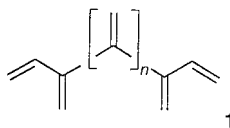
Does CIP Nomenclature Adequately
Handle Molecules with Multiple
Stereoelements? A Case Study of
Vancomycin and Cognates

Keywords: atropisomerism •
cycloisomerism • nomenclature •
stereochemistry • vancomycin

HIGHLIGHTS

Cross-conjugation is a widespread phenomenon in chemistry, especially in color chemistry. The simplest cross-conjugated organic compounds are the dendralenes with the general structure **1**. For decades these hydrocarbons only played a modest role in organic chemistry; however, the development of a general method of synthesis for **1** (up to $n = 4$) has led to the breakthrough which will enable a much more detailed investigation of the structural and chemical properties of these polyolefins.

Angew. Chem. **2001**, *113*, 727–729

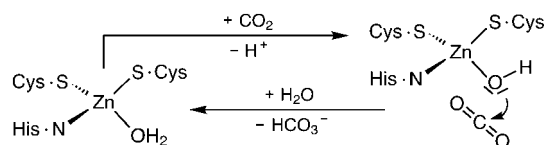


H. Hopf* 705–707

Dendralenes: The Breakthrough

Keywords: alkenes • C–C coupling •
conjugation • cycloaddition •
dendralenes

A positive biological function of the element cadmium has been established for the first time in a marine diatom which synthesizes a special cadmium carbonic anhydrase when there is a zinc deficiency. Also new is the finding that β -carbonic anhydrases of plants contain $\{Zn(N \cdot His)(S \cdot Cys)_2L\}$ centers ($L = OH_2$, $O_2C \cdot Asp$). The picture shows such a center and—greatly simplified—the probable mechanism of CO_2 hydration. It remains to be seen how closely analogous to this the cadmium center of the cadmium carbonic anhydrase is.



Angew. Chem. **2001**, *113*, 730–732

H. Strasdeit* 707–709

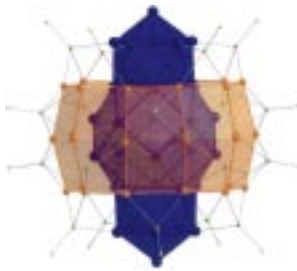
The First Cadmium-Specific Enzyme

Keywords: bioinorganic chemistry •
cadmium • enzymes • zinc

COMMUNICATIONS

New record size! The reaction of $Li[N(SiMe_3)_2]$ with a metastable solution of GaBr leads to good yields of $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$ (see picture), the largest Group 13 metalloid cluster that has been structurally characterized to date. On the basis of its highly symmetrical structure elements with predominantly covalent bonds, it is classified between the metalloid Al_{77} cluster and the fullerenes with respect to its bonding character.

Angew. Chem. **2001**, *113*, 734–737

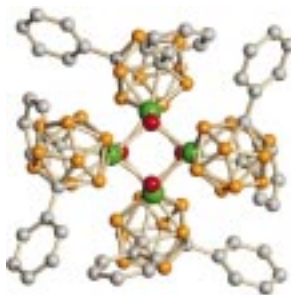


A. Schnepf, H. Schnöckel* 712–715

Synthesis and Structure of a $Ga_{84}R_{20}^{4-}$
Cluster—A Link between Metalloid
Clusters and Fullerenes?

Keywords: cluster compounds •
fullerenes • gallium • metalloid clusters •
metal–metal interactions

Monomer, dimer, trimer... now a tetrameric icosahedral metallocarborane $[\{\text{Rh}(\eta^5\text{-Ph}_2\text{C}_2\text{B}_9\text{H}_9)(\mu_3\text{-OH})\}_4]$ has been prepared as a minor by-product in the synthesis of $[1,8\text{-Ph}_2\text{-2-(1,2,3-}\eta^3\text{:5,6-}\eta^2\text{-C}_8\text{H}_{11}\text{)-closo-2,1,8-RhC}_2\text{B}_9\text{H}_9]$. The tetramer has approximate S_4 symmetry and a cubanelike $\{\text{Rh}(\text{OH})\}_4$ central core (see picture).



B. E. Hodson, D. Ellis, T. D. McGrath,
J. J. Monaghan, G. M. Rosair,
A. J. Welch * 715–717

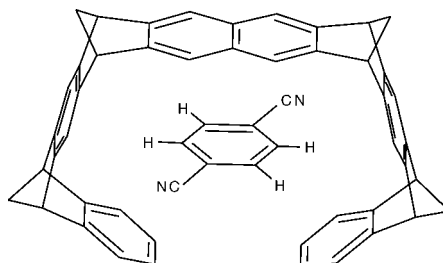
$[\{\text{Rh}(\eta^5\text{-Ph}_2\text{C}_2\text{B}_9\text{H}_9)(\mu_3\text{-OH})\}_4]$: A
Tetrameric Icosahedral Metallocarborane
Containing an $\{\text{Rh}(\text{OH})\}_4$ Cubane Cluster

Keywords: carboranes • cubanes •
metallocarboranes • rhodium

Angew. Chem. **2001**, *113*, 737–739



Together they are strong. The combination of fast MAS solid-state NMR experiments and ab initio calculations on ^1H chemical shifts allows the resolution and assignment of guest and host protons in a supramolecular complex (as shown here), provides information about motional processes, and identifies the specifics of intra- and intercomplex interactions.



S. P. Brown, T. Schaller, U. P. Seelbach,
F. Kozioł, C. Ochsenfeld, F.-G. Klärner,
H. W. Spiess * 717–720

Structure and Dynamics of the Host –
Guest Complex of a Molecular Tweezer:
Coupling Synthesis, Solid-State NMR,
and Quantum-Chemical Calculations

Keywords: ab initio calculations •
arenes • host–guest chemistry • NMR
spectroscopy • solid-state structures

Angew. Chem. **2001**, *113*, 740–743

The exchange of the methylene bridges in *p*-*t*Bu-calix[4]arene for sulfur produces a ligand seemingly perfectly suited for uranyl ions. Unlike most other metals, uranium does not bind to the four sulfur centers but is encapsulated by the ligand through binding to all four phenoxide groups (see picture). In contrast, calix[4]arene itself is dimensionally too restricted to function better than as a unidentate ligand for the uranyl ion.

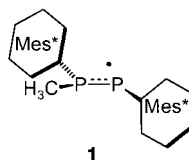


Z. Asfari, A. Bilyk, J. W. C. Dunlop,
A. K. Hall, J. M. Harrowfield,*
M. W. Hosseini, B. W. Skelton,
A. H. White 721–723

Subtleties with Sulfur: Calixarenes as
Uranophiles

Keywords: calixarenes • sulfur • uranium

Stable for at least one week below –30°C: crystals of **1**, the first highly persistent diphosphanyl radical, have been isolated and characterized. This phosphorus-centered radical exhibits hyperfine coupling whose anisotropy is considerably larger than that for well-established nitrogen radicals (hydrazyls, nitroxides). This feature is of potential interest for studies of fast molecular movements. Mes* = 2,4,6-*t*Bu₃C₆H₂.



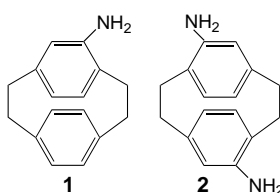
S. Loss, A. Magistrato, L. Cataldo,
S. Hoffmann, M. Geoffroy,*
U. Röhrlisberger,
H. Grützmacher * 723–726

Isolation of a Highly Persistent
Diphosphanyl Radical: The Phosphorus
Analogue of a Hydrazyl

Keywords: density functional calculations • EPR spectroscopy • phosphorus • radicals • redox chemistry

Angew. Chem. **2001**, *113*, 749–751

Polymers based on functionalized [2.2]paracyclophanes are interesting interfaces for biomedical applications. A broader application of amino[2.2]-paracyclophanes such as **1** and **2** has hitherto been limited by the lack of facile syntheses. Their effective synthesis has now been achieved in a two-step procedure in high yields.



J. Lahann, H. Höcker,
R. Langer * 726–728

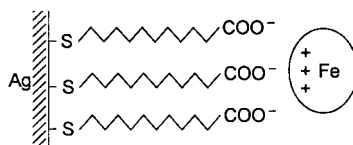
Synthesis of Amino[2.2]paracyclophanes—Beneficial Monomers for Bioactive Coating of Medical Implant Materials

Keywords: chemical vapor deposition • cyclophanes • immobilization • polymerization • superacidic systems

Angew. Chem. **2001**, *113*, 746–749

Time-resolved surface-enhanced resonance Raman spectroscopy

can selectively probe the molecular structure and dynamics of the active sites of redox proteins that are immobilized on self-assembled monolayers on Ag electrodes (see picture). As shown for the protein cytochrome *c*, this method is capable of analyzing complex interfacial processes in terms of electron transfer and non-Faradaic reactions.



D. H. Murgida,
P. Hildebrandt* 728–731

Active-Site Structure and Dynamics of Cytochrome *c* Immobilized on Self-Assembled Monolayers—A Time-Resolved Surface Enhanced Resonance Raman Spectroscopic Study

Keywords: electron transfer • heme proteins • immobilization • monolayers • Raman spectroscopy

Angew. Chem. **2001**, *113*, 751–754

The combination of two different biscatecholate ligands

with Ga^{III} ions gives rise to twelve different assemblies (shown schematically), which are all simultaneously present in solution. These were characterized by ESI-FTICR mass spectrometry and NMR spectroscopy. Even larger libraries are obtained by using an increasing number of components.



M. Ziegler, J. J. Miranda, U. N. Andersen,
D. W. Johnson, J. A. Leary,
K. N. Raymond* 733–736

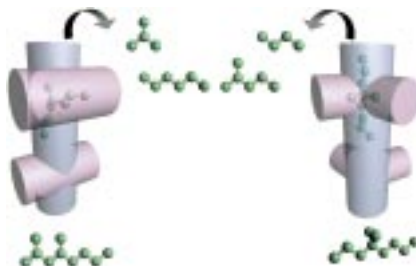
Combinatorial Libraries of Metal–Ligand Assemblies with an Encapsulated Guest Molecule

Keywords: cluster compounds • combinatorial chemistry • host–guest chemistry • self-assembly • supramolecular chemistry

Angew. Chem. **2001**, *113*, 755–758

A relatively simple reaction mechanism

for the conversion of alkanes in zeolites is obtained from molecular simulations by combining the thermodynamics with the diffusion and reaction barriers. The thermodynamics show which of the molecules will form in the zeolite, while the ultimate fate of a molecule, namely leave the zeolite or be converted (see schematic representation), depends on the relative heights of the Gibbs free energy barriers of diffusion and of subsequent reactions.



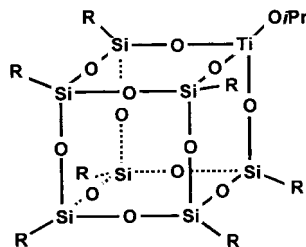
M. Schenk, B. Smit,* T. J. H. Vlucht,
T. L. M. Maesen 736–739

Shape Selectivity in Hydrocarbon Conversion

Keywords: alkanes • hydrocarbon conversion • molecular modeling • shape selectivity • zeolites

Angew. Chem. **2001**, *113*, 758–761

High-speed experimentation techniques have been applied in the synthesis and testing of silsesquioxane-based titanium catalysts (see picture) for the epoxidation of alkenes. Different solvents and organotrichlorosilanes were employed in the optimization of the hydrolytic condensation of silanes to open silsesquioxane structures. This new, fast, and simple synthesis route yields catalysts whose performance is comparable to the best known silsesquioxane-based titanium catalysts.



P. P. Pescarmona, J. C. van der Waal,
I. E. Maxwell, T. Maschmeyer* 740–743

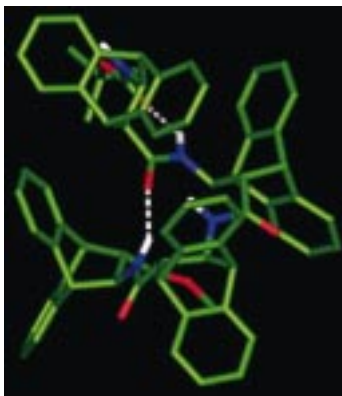
A New, Efficient Route to Titanium–Silsesquioxane Epoxidation Catalysts Developed by Using High-Speed Experimentation Techniques

Keywords: catalysts • epoxidation • high-throughput synthesis • silsesquioxanes • titanium

Angew. Chem. **2001**, *113*, 762–765

A twelve-membered hydrogen-bonded ring and the resulting helical structure (see picture) in the tetrapeptide and an eight-membered hydrogen-bonded ring in the dipeptide illustrate the structural consequences of the incorporation of the novel β -amino acid derived from the Diels–Alder adduct of anthracene and dimethyl fumarate.

Angew. Chem. **2001**, *113*, 765–767



J. D. Winkler,* E. L. Piatnitski,
J. Mehlmann, J. Kaspárec,
P. H. Axelsen* 743–745

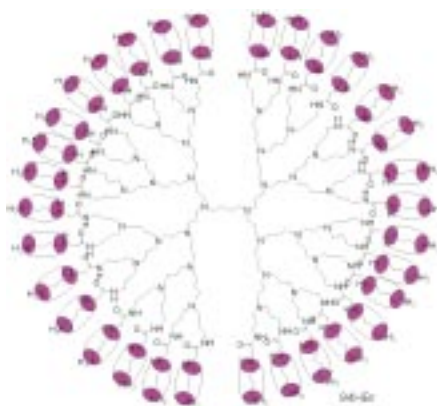
Design and Synthesis of Foldamers Based
on an Anthracene Diels–Alder Adduct

Keywords: amino acids • asymmetric
synthesis • conformation analysis •
peptidomimetics



Thirty-two molecular beads are threaded onto the terminal groups of a fourth-generation dendrimer (see picture). These pseudorotaxane-terminated dendrimers not only constitute a new class of topologically intriguing molecules but also provide a novel way of modifying dendrimer exteriors by noncovalent interactions.

Angew. Chem. **2001**, *113*, 769–771



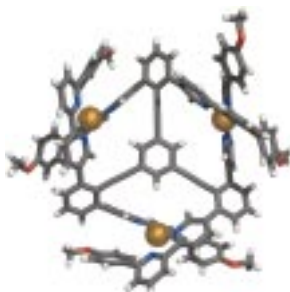
J. W. Lee, Y. H. Ko, S.-H. Park,
K. Yamaguchi, K. Kim* 746–749

Novel Pseudorotaxane-Terminated
Dendrimers: Supramolecular
Modification of Dendrimer Periphery

Keywords: dendrimers • noncovalent
interactions • rotaxanes • supramolecular
chemistry

The construction of molecules such as knots and links can be facilitated by using metal–ligand coordination complexes as template structures; however, the control of the stereochemistry by cooperative steric interactions among metal–ligand sites remains a challenge. A simple, but general, cantilever control mechanism is demonstrated here through the stereoselective synthesis of a trinuclear copper(I)-bipyridine triskelion (see picture).

Angew. Chem. **2001**, *113*, 771–773



C. R. Woods, M. Benaglia, S. Toyota,
K. Hardcastle, J. S. Siegel* 749–751

Trinuclear Copper(I)-bipyridine
Triskelion: Template/Bascule Control of
Coordination Complex Stereochemistry
in a Trefoil Knot Precursor

Keywords: coordination chemistry •
molecular design • stereochemistry •
supramolecular chemistry

Design principles in polynuclear coordination complexes have been based on the idea that metal ions would acquire donor atoms up to the metal's ligand field preference, and donor ligands, such as 1,10-phenanthroline, would not leave donor atoms uncoordinated to a metal ion. The geometry of the simple molecular grid formed from a series of 3,3'-biphenanthrolines complexed with Cu^{I} or Ag^{I} ions sets up a cleft that binds uncoordinated ligands through a combination of intercalation, solvation, and CH-to-N interactions (see picture).

Angew. Chem. **2001**, *113*, 773–776



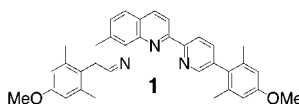
S. Toyota, C. R. Woods, M. Benaglia,
R. Haldimann, K. Wärnmark,
K. Hardcastle, J. S. Siegel* 751–754

Tetranuclear Copper(I)-Biphenanthroline
Gridwork: Violation of the Principle of
Maximal Donor Coordination Caused by
Intercalation and CH-to-N Forces

Keywords: coordination chemistry •
molecular design • stereochemistry •
supramolecular chemistry



As a hybrid of two aryl motifs, that is *p*-anisyl and mesityl, the 4-methoxy-2,6-dimethylphenyl or “manisyl” substituent offers possibilities for both further structural elaboration as well as enhancing the solubility of the heterocyclic ligands mentioned in the title. A highlight of this work lies in the ability of the manisyl group to endow specific members of this family such as **1** with high fluorescence quantum efficiency.



Angew. Chem. **2001**, *113*, 776–779

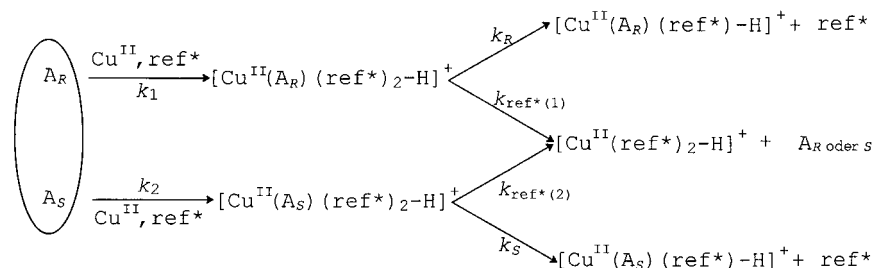
J. C. Loren, J. S. Siegel* 754–757

Synthesis and Fluorescence Properties of Manisyl-Substituted Terpyridine, Bipyridine, and Phenanthroline

Keywords: fluorescence • ligand design • N ligands • nitrogen heterocycles



Independent parallel ion/molecule reactions and fast dissociation have been used to quantify small enantiomeric excesses of dipeptides in a new mass-spectrometric method. The *ee* values are determined by simply mixing the analyte with CuCl₂ and a chiral reference compound (ref*) in aqueous methanol and observing the relative abundances of the diastereomeric cluster ions (see scheme).



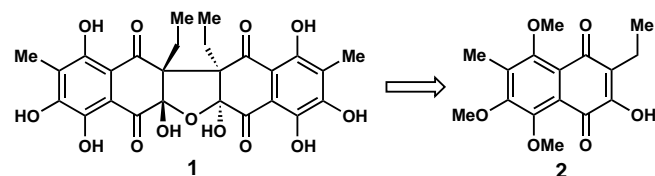
Angew. Chem. **2001**, *113*, 779–782

W. A. Tao, R. G. Cooks* 757–760

Parallel Reactions for Enantiomeric Quantification of Peptides by Mass Spectrometry

Keywords: chiral resolution • kinetics • mass spectrometry • peptides

A radical-based dimerization approach starting with naphthazarin **2** furnished the lichen-derived title compound **1** in racemic form. This cascade strategy, or a closely related variant of it, may not be too dissimilar to the pathway adopted by nature in the biosynthesis of this natural product which shows potent cytotoxic properties.



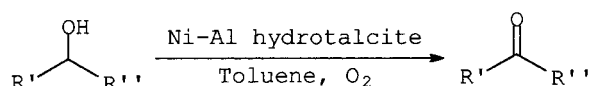
Angew. Chem. **2001**, *113*, 783–785

K. C. Nicolaou,* D. Gray 761–763

Total Synthesis of Hybocarpone

Keywords: natural products • oxidative coupling • photochemistry • quinones • total synthesis

NiO in association with aluminum oxide has been identified by temperature-programmed reduction as the active species in the Ni–Al hydrotalcite catalyst that oxidizes α -ketols as well as benzylic and allylic alcohols to their corresponding carbonyl compounds in oxygen in quantitative yields under mild reaction conditions (see scheme).



Angew. Chem. **2001**, *113*, 785–788

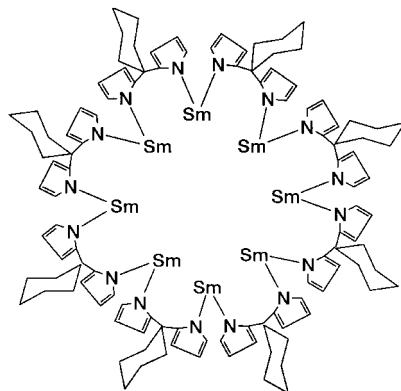
B. M. Choudary,* M. L. Kantam, A. Rahman, C. V. Reddy, K. K. Rao 763–766

The First Example of Activation of Molecular Oxygen by Nickel in Ni–Al Hydrotalcite: A Novel Protocol for the Selective Oxidation of Alcohols

Keywords: alcohols • hydrotalcites • oxidation • oxygen • reduction

Transamination reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}(\text{thf})_2$ with the dianion of either 1,1-di-(α -pyrrolyl)-cyclohexane or diphenyl dipyrromethane led to the octanuclear complex shown in the picture and the hexanuclear complex $[[\text{Ph}_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2]\text{Sm}]_6(\text{thf})_3$, respectively. Both clusters possess flat macrocyclic structures and react with dinitrogen to afford the corresponding isostructural tetranuclear dinitrogen complexes.

Angew. Chem. **2001**, *113*, 788–791



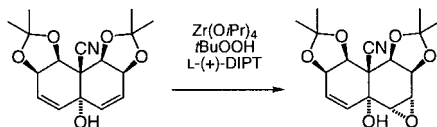
M. Ganesan, S. Gambarotta,*
G. P. A. Yap 766–769

Highly Reactive Sm^{II} Macrocyclic
Clusters: Precursors to N_2 Reduction

Keywords: N ligands • N_2 complexes •
nitrogen fixation • samarium



Zirconium to the rescue! Eight contiguous chiral centers can be established with >95% *ee* in the key step of an asymmetric synthetic approach to the cores of certain *Celastraceae* sesquiterpenes (see scheme). The route required the development of a new zirconium-modified Sharpless asymmetric epoxidation instead of the traditional titanium version. DIPT = diisopropyl tartrate.



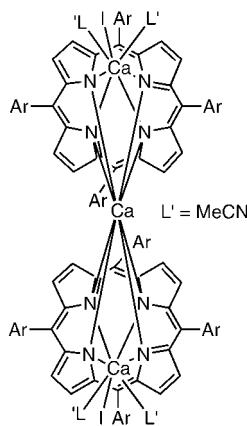
A. C. Spivey,* S. J. Woodhead,
M. Weston, B. I. Andrews 769–771

Enantioselective Desymmetrization of
meso-Decalin Diallylic Alcohols by a New
Zr-Based Sharpless AE Process: A Novel
Approach to the Asymmetric Synthesis of
Polyhydroxylated *Celastraceae*
Sesquiterpene Cores

Keywords: asymmetric catalysis •
desymmetrization • epoxidation •
natural products • zirconium

Angew. Chem. **2001**, *113*, 791–793

Unexpected salt-carrier properties are displayed by the calcium porphyrin presented here. The treatment of the free porphyrin with activated calcium metal gives a 1:1 complex in which the calcium ion is coordinatively unsaturated. Addition of $[\text{CaI}_2(\text{thf})]$ then results in the formation of a double-decker structure (see picture, Ar = *tert*-butylphenyl), which has been characterized by X-ray crystallographic analysis.



L. Bonomo, M.-L. Lehaire, E. Solari,
R. Scopelliti, C. Floriani* 771–774

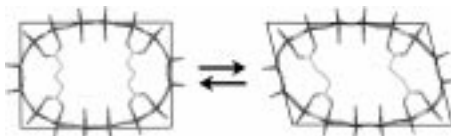
The First Crystalline Calcium Porphyrin
and Tetrakis(*tert*-butylphenyl)por-
phyrinato Calcium(II): Its Synthesis,
Structure, and Binding Properties
Towards Alkali and Alkaline Earth Metal
Salts

Keywords: calcium • NMR spectroscopy
• porphyrinoids • salt effect • structure
elucidation

Angew. Chem. **2001**, *113*, 793–796

**The largest discrete cyclic oxo-
thioanion**

$[\text{W}_{16}\text{S}_{16}\text{O}_{16}(\text{OH})_{16}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_6\text{O}_4)_2]^{4-}$ was prepared by acido–basic self-condensation of the $[\text{W}_2\text{O}_2\text{S}_2]^{2+}$ building block in the presence of glutarate ions $[\text{C}_5\text{H}_6\text{O}_4]^{2-}$. The solid-state characterization (X-ray diffraction) revealed two conformations for the templated-ring which can be viewed as two snapshots of the dynamic of the wheel in solution (see picture). The ion was also characterized in aqueous solution by ^1H NMR and Raman spectroscopies.



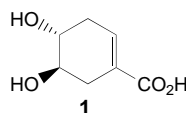
E. Cadot,* J. Marrot,
F. Sécheresse 774–777

$[\text{W}_{16}\text{S}_{16}\text{O}_{16}(\text{OH})_{16}(\text{H}_2\text{O})_4(\text{C}_5\text{H}_6\text{O}_4)_2]^{4-}$:
A Flexible, Pillared Oxothiotungstate
Wheel

Keywords: carboxylato complexes •
polyanions • sulfur • template synthesis •
tungsten

Angew. Chem. **2001**, *113*, 796–799

Competition feeding experiments performed in vivo have identified **1** as the true starter unit for the rapamycin polyketide synthase, and indicate its potential application for generating novel analogues of this clinically important immunosuppressant molecule.



P. A. S. Lowden, B. Wilkinson,
G. A. Böhm, S. Handa, H. G. Floss,
P. F. Leadlay, J. Staunton* 777–779

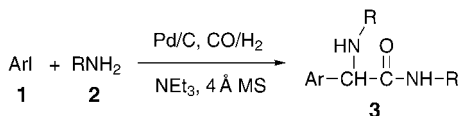
Origin and True Nature of the Starter Unit for the Rapamycin Polyketide Synthase

Keywords: biosynthesis • isotopic labeling • natural products • polyketides • reaction mechanisms

Angew. Chem. **2001**, *113*, 799–801



A new domino reaction sequence, a palladium-catalyzed double carbonylhydroamination, which involves double carbonylation, amine condensation, and hydrogenation from an aryl iodide (**1**), a primary amine (**2**), and synthetic gas has been realized as a novel synthetic means for the one-pot synthesis of α -amino amides (**3**).



Y.-S. Lin, H. Alper* 779–781

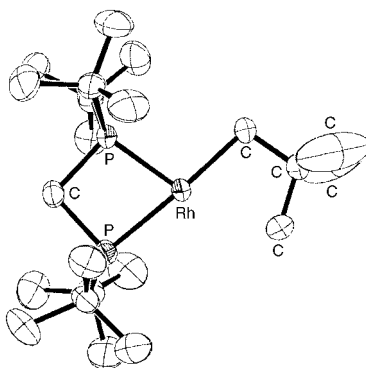
A Novel Approach for the One-Pot Preparation of α -Amino Amides by Pd-Catalyzed Double Carbonylhydroamination

Keywords: amination • amino amides • carbonylation • domino reactions • hydrogenation

Angew. Chem. **2001**, *113*, 801–803



γ -C–H agostic stabilization of the 14-electron metal center by a saturated hydrocarbon group characterizes the structure of the first neutral, three-coordinate alkylrhodium(I) complex $[(\kappa^2\text{-dtbpm})\text{RhNp}]$ (**1**; dtbpm = bis(di-*tert*-butylphosphanyl)methane, Np = neopentyl). Some of its reactions, for example, N_2 complexation and C–H bond activation, are reported.



H. Urtel, C. Meier, F. Eisenträger,
F. Rominger, J. P. Joschek,
P. Hofmann* 781–784

A Neutral Three-Coordinate Alkylrhodium(I) Complex: Stabilization of a 14-Electron Species by γ -C–H Agostic Interactions with a Saturated Hydrocarbon Group

Keywords: agostic interactions • C–H activation • density functional calculations • rhodium

Angew. Chem. **2001**, *113*, 803–806

Appreciable oxygen permeability at elevated temperatures (650–850°C) allows the well-known high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ to be used as an oxygen separation membrane. Permeation of air through a $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ disk 1.2 mm thick gave an O_2 stream in which N_2 was barely detectable by gas chromatography. This technology may have potential applications in high-temperature oxygen-based industrial processes.

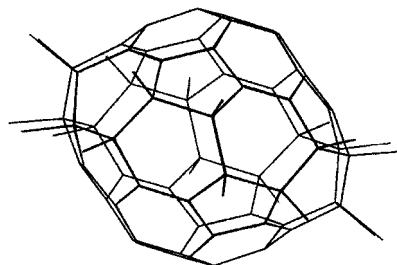
C.-s. Chen,* S. Ran, W. Liu, P.-h. Yang,
D.-k. Peng,
H. J. M. Bouwmeester 784–786

$\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ as an Oxygen Separation Membrane

Keywords: membranes • oxygen separation • perovskite phases • superconductors

Angew. Chem. **2001**, *113*, 806–808

Flattened poles and an expanded equator reminiscent of a spinning planet characterize the cage structure of D_{5d} $\text{C}_{60}\text{F}_{20}$ (“saturnene”, see picture) which is based on two dehydrocorannulene moieties bound together by a $(\text{CF})_{20}$ chain. $\text{C}_{60}\text{F}_{20}$ was isolated from the reaction of C_{60} with K_2PtF_6 in a vacuum at 470°C. The ^{19}F NMR spectrum shows a single line at $\delta = -132.8$. The unique structure of $\text{C}_{60}\text{F}_{20}$ suggests use as a synthon for derivatives having donor–acceptor properties.



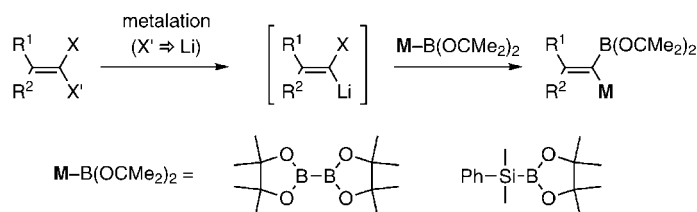
O. V. Boltalina,* V. Yu. Markov,
P. A. Troshin, A. D. Darwish, J. M. Street,
R. Taylor* 787–789

$\text{C}_{60}\text{F}_{20}$: “Saturnene”, an Extraordinary Squashed Fullerene

Keywords: fluorine • fullerenes • NMR spectroscopy • polyaddition

Angew. Chem. **2001**, *113*, 809–811

A 1,2-migration of a boryl or silyl group with inversion of configuration occurs in the reaction of alkylidene-type lithium carbenoids with diboron or silylborane derivatives to give the corresponding 1,1-diboryl- or 1-boryl-1-silylalkenes in good yields (see scheme).



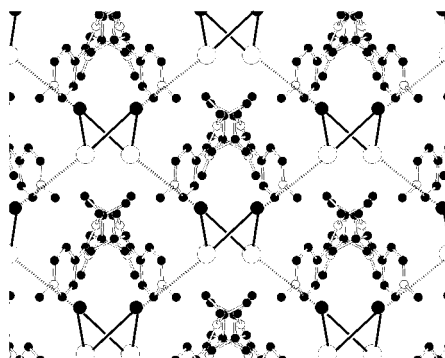
Angew. Chem. **2001**, *113*, 812–814

T. Hata, H. Kitagawa, H. Masai,
T. Kurahashi, M. Shimizu,*
T. Hiyama * 790–792

Geminal Difunctionalization of
Alkenylidene-Type Carbenoids by Using
Interelement Compounds

Keywords: borates • carbenoids •
metalations • palladium •
rearrangements

Stable free radicals can be trapped inside a three-dimensional (3D) inorganic network. The formation of a new type of mixed-metal oxalate $[\text{Mn}^{\text{II}}(\text{H}_2\text{O})\text{Cr}^{\text{III}}(\text{ox})_3]^-$ is induced by the presence of a cationic nitronyl nitroxide radical (rad^+). The figure shows a stylized view of the 3D network $\circ = \text{Mn}$, $\bullet = \text{Cr}$. This hybrid organic–inorganic compound behaves as an antiferromagnet at 6 K.



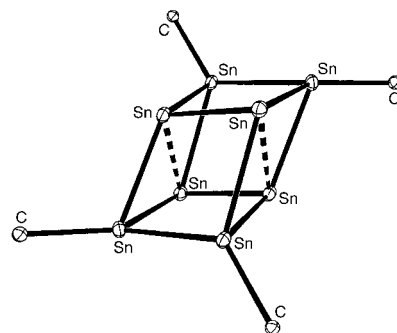
Angew. Chem. **2001**, *113*, 814–817

G. Ballester, E. Coronado,*
C. Giménez-Saiz,
F. M. Romero * 792–795

Nitroxide Radicals as Templating Agents
in the Synthesis of Magnets Based on
Three-Dimensional Oxalato-Bridged
Heterodimetallic Networks

Keywords: crystal engineering • host–
guest chemistry • magnetic properties •
organic–inorganic hybrid composites •
radicals

A distorted rhombic-prismatic arrangement, previously unobserved for a main group metal cluster, is present in $[\text{Sn}_8(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_4]$ (see structure; only the *ipso*-C atoms of the ligands are shown), which was obtained by reduction of $[\{\text{Sn}(\mu\text{-Cl})(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\}_2]$ with potassium in THF. Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$.



Angew. Chem. **2001**, *113*, 818–819

B. E. Eichler, P. P. Power * 796–797

Synthesis and Characterization of
 $[\text{Sn}_8(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_4]$ (Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$): A Main Group Metal Cluster
with a Unique Structure

Keywords: C ligands • cluster com-
pounds • low-valent compounds •
terphenyls • tin



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

* Author to whom correspondence should be addressed



BOOKS

The Weak Hydrogen Bond

Gautam R. Desiraju, T. Steiner

J. Elguero 799

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Chemistry of Natural Products and
Their Model Compounds**

Jürgen-Hinrich Fuhrhop, C. Endisch

A. Davis 800

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Issue 3, 2001 was published online on January 30, 2001.

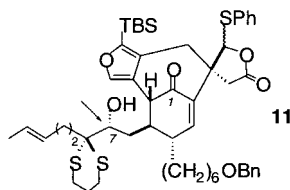
Don't forget all the Tables of Contents from 1995 onwards may be still found on the WWW under:
<http://www.angewandte.com>

CORRIGENDA

In the Communication by **S. Danishefsky et al.** in Issue 20, 2000, pp. 3652–3656 the acknowledgements should include the following: Z.-G.W. thanks the US Army for a postdoctoral fellowship (DAMD 7-97-1-7119).

The $\pi^*(\text{FeO})$ orbitals in Scheme 2 of the Communication by **S. Shaik et al.** in Issue 21, 2000, pp. 3851–3855 were incorrectly described: they should be d_{xy} and d_{yz} instead of d_{xy} and d_{yz} .

The structural formula of compound **11** in the Communication by **S. Danishefsky et al.** Issue 24, 2000, pp. 4509–4511 contains two errors: a sulfur atom is missing in the dithiane ring and a hydroxyl group is wrongly placed at C1. The correct formula is given here.



The product in Equation (1) in the Communication by **G. C. Fu et al.** in Issue 1, 2001, pp. 234–236 contains one too many hydrogen atoms at the nitrogen atom. The correct version of the Equation is shown here.

