ANGEWANDTE
CHEMIE
A Journal of the
Gesellschaft
Deutscher Chemiker
INTERNATIONAL EDITION
2002
41/24
Pages 4595–4802

Cover Picture
of the Year
Cast your vote at
www.angewandte.org
and win a great book!

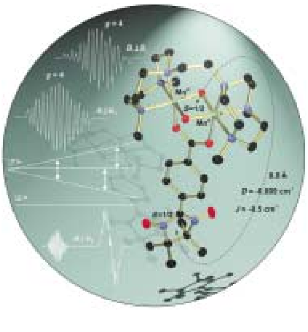
The editorial staff and the publishers thank all readers, authors, referees, and advertisers for their interest and support over the past year and wish them all a happy new year.

Editorial Note

In 2002 there were 26 issues of *Angewandte Chemie International Edition*, two of which were indexes: in Spring there was an index of all the Reviews from the last 40 years; this appeared without an issue number. With this current issue (No. 24) the Annual Index for 2002 is included as a separate issue. This Annual Index should be bound with the other issues. However, for the 40-Year Index, which has its own separate page numbering, this is not necessary. **Copies of the 40-Year Index can be obtained at the special price of € 19.80 (including postage) from the Editorial Office.**

COVER PICTURE

The cover picture shows the structure of a paramagnetic dimanganese complex tethered to a distant organic radical. The long-distance magnetic interaction between the two $S=1/2$ centers in this complex models a similar situation detected in the $S_2Y_z^{\bullet}$ state of photosystem II (PSII). In their article on page 4775, D. S. Marlin, E. Bill, and K. Wieghardt et al. shed light on the nature of this interaction through the use of SQUID magnetic measurements as well as dual-mode X-band EPR spectroscopy. One of the most remarkable features observed from such dual-mode EPR measurements is the identification of well-resolved "forbidden" half-field multiline signals at $g=4$ that arise from the dipolar coupling. This latter feature may also be noteworthy in the context of a poorly understood signal at $g=4.1$ that has been observed in various EPR spectra of PSII.



1433-7851/02/4124-4597 $ 20.00+.50/0

M. Quack* 4618–4630

How Important is Parity Violation for Molecular and Biomolecular Chirality?

Far more important (by orders of magnitude) than previously believed: this is the answer to the question in the title according to calculations based on recently introduced methods of electroweak quantum chemistry. However, the energy differences between enantiomers of chiral molecules are still very small, on the order of pico- to femtojoules per mole. This review covers the following aspects of parity violation: How can such small energies be measured and what are the consequences for our understanding of molecular chirality, biomolecular homochirality, and perhaps fundamental physics?

Angew. Chem. **2002**, *114*, 4812–4825

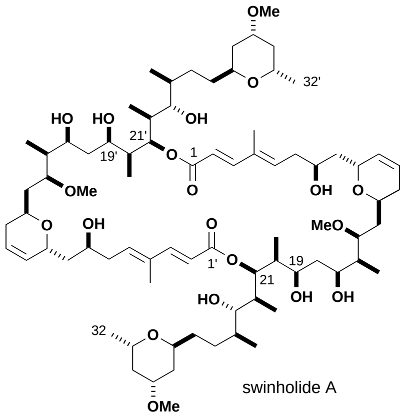
Keywords: biological homochirality · chirality · parity violation · symmetries

---

K.-S. Yeung,* I. Paterson ... 4632–4653

Actin-Binding Marine Macrolides: Total Synthesis and Biological Importance

Marine organisms provide a rich source of highly functionalized macrolides (such as swinholide A) that interact with the actin cytoskeleton by mechanisms similar to actin-binding proteins. Total syntheses of these potent cytotoxic natural products have been accomplished recently, making use of a variety of strategies for introducing the multiple stereogenic centers and constructing the characteristic 22- to 44-membered macrocycles.



swinholide A

Angew. Chem. **2002**, *114*, 4826–4847

Keywords: actin · antitumor agents · macrolides · natural products · total synthesis

---

VIPs

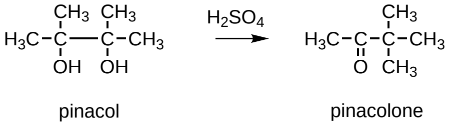
The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly. Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.org

Tuning the Regioselectivity in the Palladium(II)-Catalyzed Isomerization of Alkylidenecyclopropyl Ketones: A Dramatic Salt Effect	S. Ma*, J. Zhang
Porphyrazines as Molecular Scaffolds: Periphery–Core Spin Coupling Between Metal Ions of a Schiff Base Porphyrazine	M. Zhao, C. Stern, A. G. M. Barrett,* B. M. Hoffman*
Beyond the Icosahedron: The First 13-Vertex Carborane	A. Burke, D. Ellis, B. T. Giles, B. E. Hodson, S. A. Macgregor, G. M. Rosair, A. J. Welch*
Topomerization of a Distorted-Rhomboid Tetraborane(4) and its Hydroboration to a Pentaborane(7)	C. Präsang, M. Hofmann, G. Geiseler, W. Massa, A. Berndt*
A New Diversity-Oriented Synthesis of α-Amino Acid Derivatives by a Silyltelluride-Mediated Radical Coupling Reaction of Imines and Isonitriles	S. Yamago,* H. Miyazoe, T. Nakayama, M. Miyoshi, J. Yoshida*
Facile Solid-State Synthesis of Highly Conducting Poly(ethylenedioxythiophene)	H. Meng, D. F. Perepichka, F. Wudl*
[3+2]/[4+1] Cycloaddition Reactions of Fischer Alkoxy(alkenyl)carbene Complexes with Electronically Neutral 1,3-Dienes	J. Barluenga,* S. López, J. Flórez
Salinosporamide A, a Highly Cytotoxic Proteasome Inhibitor from a Novel Microbial Source, a Marine Bacterium of the New Genus *Salinospora*	R. H. Feling, G. O. Buchanan, T. J. Mincer, C. A. Kauffman, P. R. Jensen, W. Fenical*
New Open-Network Architectures from the Self-Assembly of $AgNO_3$ and 5,10,15,20-Tetra(4-pyridyl)porphyrin Building Blocks: The Exceptional Self-Penetrating Topology of the 3D Network of $[Ag_8(Zn^{II}tpyp)_7(H_2O)_2](NO_3)_8$	L. Carlucci, G. Ciani,* D. M. Proserpio, F. Porta
Large Parity Violation Effects in Heavy-Metal-Containing Chiral Compounds	P. Schwerdtfeger,* J. Gierlich, T. Bollwein
Cyanide-Bridged Iron(III)-Cobalt(II) Double Zigzag Ferromagnetic Chains: Two New Molecular Magnetic Nanowires	R. Lescouëzec, J. Vaissermann, C. Ruiz-Pérez, F. Lloret, R. Carrasco, M. Julve,* M. Verdaguer,* Y. Dromzee, D. Gatteschi, W. Wernsdorfer

1433-7851/02/4124-4598 $ 20.00+.50/0

ESSAY

Radical changes in the chemical community's thinking were required in the discovery of the pinacol rearrangment [Eq. (a)]. Clarity was achieved only after the incorrect "conventional" atomic weights, which gave completely erroneous molecular formulas, were rejected and people dared to violate Kekulé's rules of reaction concerning the connectivity of the carbon skeleton in chemical reaction.



$$H_3C-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow{H_2SO_4} H_3C-\underset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \qquad (a)$$

Angew. Chem. **2002**, *114*, 4848 – 4854

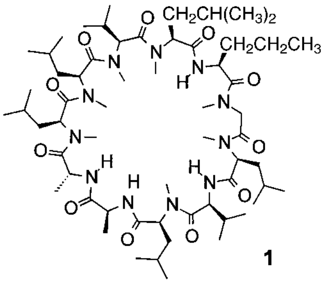
J. A. Berson* .... 4655 – 4660

What Is a Discovery? Carbon Skeletal Rearrangements as Counter-Examples to the Rule of Minimal Structural Change

Keywords: carbon · history of chemistry · pinacol · rearrangement · structure elucidation

HIGHLIGHTS

An efficient coupling reaction in peptide chemistry is achieved through the use of Fmoc-protected amino acid chlorides generated in situ. This method permits racemization-free incorporation of *N*-methyl amino acids into peptides, as could be shown in the syntheses of cyclosporin O (**1**) and omphalotin A.



1

Angew. Chem. **2002**, *114*, 4855 – 4857

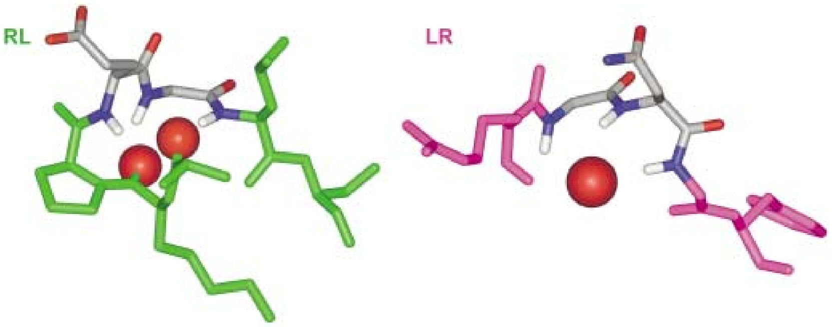
N. Sewald* .... 4661 – 4663

Efficient, Racemization-Free Peptide Coupling of *N*-Alkyl Amino Acids by Using Amino Acid Chlorides Generated In Situ—Total Syntheses of the Cyclopeptides Cyclosporin O and Omphalotin A

Keywords: amino acids · bioorganic chemistry · coupling reagent · peptides · total synthesis · triphosgene

---

Protein structure prediction, not only description: A step in this direction is the discovery that many anion and cation binding sites (where ions can be atoms exhibiting a full or partial charge) in proteins are made up of three amino acids of which two exhibit "enantiomeric" main-chain conformations. The combination of torsion angle pairs determines whether an RL or an LR nest is formed (see picture).



Angew. Chem. **2002**, *114*, 4857 – 4860

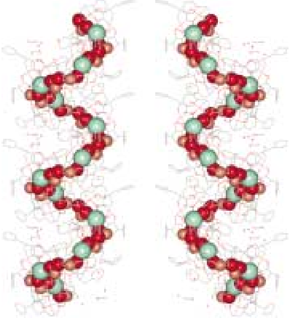
D. Pal, J. Sühnel,*
M. S. Weiss* .... 4663 – 4665

New Principles of Protein Structure: Nests, Eggs—and What Next?

Keywords: protein structures · structural bioinformatics · structural motifs

COMMUNICATIONS

The chirality of the ligand determines the nature of the helix: Coordination of a chain of [15]metallacrown-5 complexes based on phenylalanine hydroxamic acid results in an amphiphilic metallohelix with a 4_1 screw axis. The use of the L isomer of the acid gives the right-handed helix (see left structure) while the D isomer gives the mirror image structure.



Angew. Chem. **2002**, *114*, 4862 – 4864

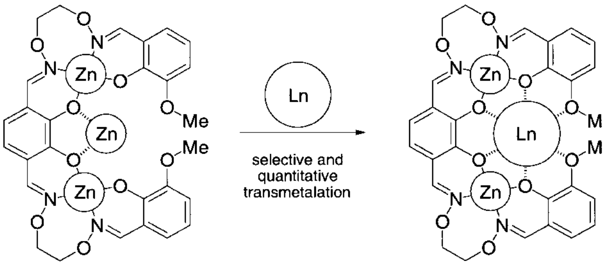
A. D. Cutland-Van Noord, J. W. Kampf,
V. L. Pecoraro* .... 4667 – 4670

Preparation of Resolved Fourfold Symmetric Amphiphilic Helices Using Chiral Metallacrown Building Blocks

Keywords: copper · crown compounds · helical structures · lanthanides · supramolecular chemistry

1433-7851/02/4124-4599 $ 20.00+.50/0

Only the central metal atom of the homotrinuclear complex $[LZn_3]^{2+}$, prepared by cooperative complexation between a linear ligand and $Zn(OAc)_2$, is replaced with a Ln^{3+} ion by selective and quantitative transmetalation to give a helical heterotrinuclear complex $[LZn_2Ln]^{3+}$ (see scheme). Ln = lanthanide.



Angew. Chem. **2002**, *114*, 4864–4867

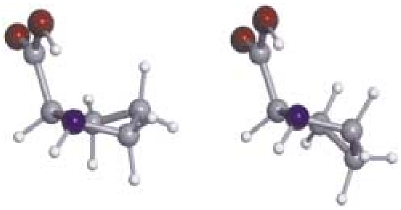
S. Akine, T. Taniguchi,
T. Nabeshima* 4670–4673

Novel Synthetic Approach to Trinuclear 3d-4f Complexes: Specific Exchange of the Central Metal of a Trinuclear Zinc(II) Complex of a Tetraoxime Ligand with a Lanthanide(III) Ion

Keywords: cooperative phenomena • host–guest systems • lanthanides • N,O ligands • transmetalation

---

An intramolecular hydrogen bond of the type OH···N is present in both conformers of proline (see picture) that were observed in the gas phase using laser-ablation molecular-beam Fourier-transform microwave spectroscopy.



Angew. Chem. **2002**, *114*, 4867–4870

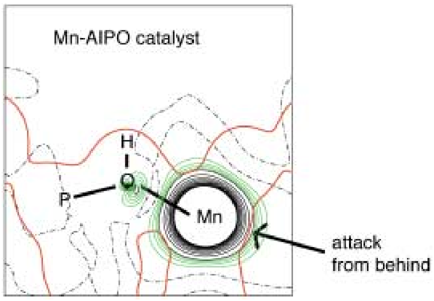
A. Lesarri, S. Mata, E. J. Cocinero,
S. Blanco, J. C. López,
J. L. Alonso* 4673–4676

The Structure of Neutral Proline

Keywords: amino acids • conformational analysis • laser chemistry • rotational spectroscopy

---

Periodic quantum mechanical calculations on transition-metal-doped AlPO-34 show that the Lewis acidity is linked to the electronic distribution at the transition metal site. A "from behind" attack of 2+ dopant ions by Lewis bases is favored (see picture), and is expected to yield stronger Lewis acidity for polymorphs with single-wall framework structures or intersecting channels, rather than polymorphs with one-dimensional channels that are composed solely of double-walled structural units.



Angew. Chem. **2002**, *114*, 4871–4874

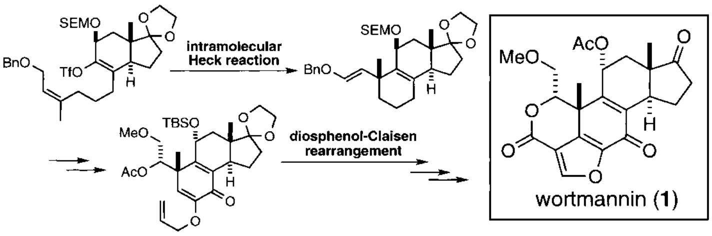
F. Corà,* I. Saadoune,
C. R. A. Catlow 4677–4680

Lewis Acidity in Transition-Metal-Doped Microporous Aluminophosphates

Keywords: ab initio calculations • density functional calculations • heterogeneous catalysis • Lewis acids • zeolite analogues

---

A potent and specific phosphoinositide 3-kinase inhibitor (±)-wortmannin has been achieved through an intramolecular Heck reaction for the construction of an allylic quaternary carbon center and a diosphenol–Claisen rearrangement (see scheme). SEM = 2-(Trimethylsilyl)ethoxymethyl.



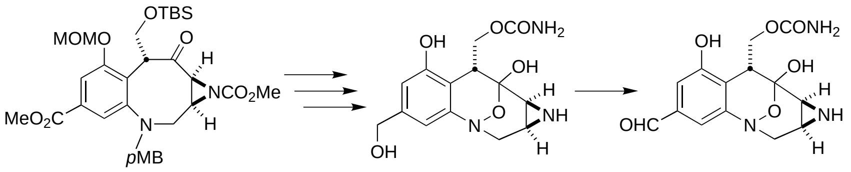
Angew. Chem. **2002**, *114*, 4874–4876

T. Mizutani, S. Honzawa, S.-y. Tosaki,
M. Shibasaki* 4680–4682

Total Synthesis of (±)-Wortmannin

Keywords: Heck reaction • natural products • phosphoinositide 3-kinase • rearrangement • total synthesis

The remarkable one-step deprotection/oxidative cyclization of an eight-membered-ring aminoketone **1** in the presence of dimethyldioxirane gives rise to the unique hydroxylamine hemiketal ring system of FR66979 (**2**) and FR900482 (**3**), clinically important antitumor antibiotics. The concise 33-step enantioselective synthesis of **3** is the shortest route reported to date.



1 **2** **3**

Angew. Chem. **2002**, *114*, 4877–4879

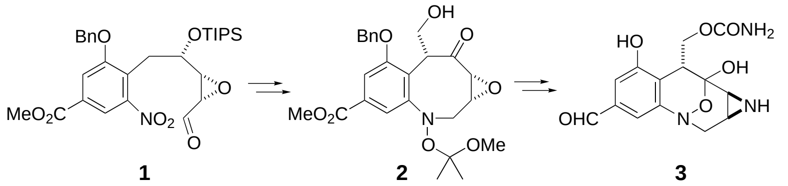
T. C. Judd, R. M. Williams* 4683–4685

Concise Enantioselective Synthesis of (+)-FR66979 and (+)-FR900482: Dimethyldioxirane-Mediated Construction of the Hydroxylamine Hemiketal

Keywords: antitumor agents · asymmetric synthesis · hydroxylamines · natural products · total synthesis

---

Intramolecular hydroxylamination of ω-formyl nitrobenzene **1** followed by stereoselective hydroxymethylation led to the formation of *N*-hydroxybenzazocine **2**, a key intermediate in the enantioselective total synthesis of the antitumor antibiotic FR900482 (**3**).



1 **2** **3**

Angew. Chem. **2002**, *114*, 4880–4882

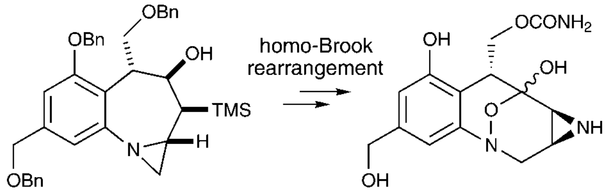
M. Suzuki, M. Kambe, H. Tokuyama, T. Fukuyama* 4686–4688

Facile Construction of *N*-Hydroxybenzazocine: Enantioselective Total Synthesis of (+)-FR900482

Keywords: aldol reaction · antitumor agents · asymmetric synthesis · hydroxylamines · natural products · total synthesis

---

An unusual fragmentation of aziridine 1, triggered by a preliminary homo-Brook transposition is the key step in the total synthesis of the racemate of the antitumor agent FR66979 (**2**).



1 **2**

Angew. Chem. **2002**, *114*, 4882–4885

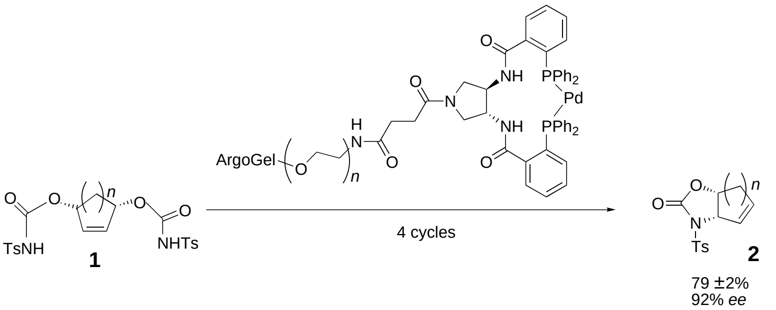
R. Ducray, M. A. Ciufolini* 4688–4691

Total Synthesis of (±)-FR66979

Keywords: antitumor agents · asymmetric synthesis · natural products · rearrangement · total synthesis

---

The choice of scaffold and tether has a marked influence on the enantiomeric excesses obtained in Pd-catalyzed asymmetric allylic alkylations, such as the cyclization of the bisurethane **1** to the oxazolidin-2-one **2** [Eq. (1); Ts = *p*-toluenesulfonate], performed with polymer-supported chiral catalysts. The best results were obtained by using an ArgoGel resin, an amide tether, and a pyrrolidine scaffold.



(1)

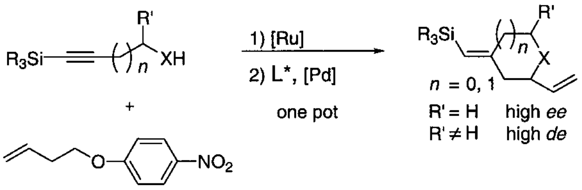
Angew. Chem. **2002**, *114*, 4885–4887

B. M. Trost,* Z. Pan, J. Zambrano, C. Kujat 4691–4693

Polymer-Supported C_2-Symmetric Ligands for Palladium-Catalyzed Asymmetric Allylic Alkylation Reactions

Keywords: allylic alkylation · asymmetric synthesis · N ligands · palladium · polymer-supported catalysts

Five- and six-membered nitrogen and oxygen heterocycles are accessible from two acyclic precursors in a one-pot reaction that comprises a Ru-catalyzed ene–yne addition followed by a Pd-catalyzed asymmetric allylic alkylation (see scheme). The stereochemistry of the products derives from the catalyst rather than from substrate control using chiral substrates.

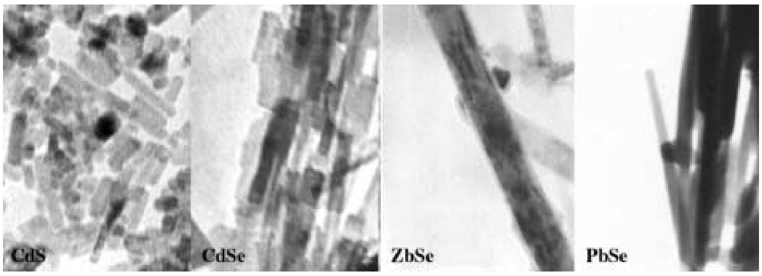


Angew. Chem. **2002**, *114*, 4887–4891

Keywords: alkylation · asymmetric synthesis · heterocycles · homogeneous catalysis · palladium · ruthenium

---

Solvothermal synthesis in a monodentate ligand, namely, *n*-butylamine, is a general route for the synthesis of semiconductor chalcogenide nanorods from cheap inorganic reactants. The amine proved to be a good shape controller for producing CdS, CdSe, ZnSe, and PbSe nanorods (see picture) under relatively mild conditions.

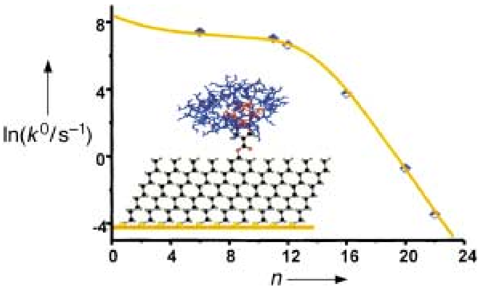


Angew. Chem. **2002**, *114*, 4891–4894

Keywords: crystal growth · nanostructures · semiconductors · solvothermal synthesis

---

Directly linking a gold electrode coated with pyridine-terminated self-assembled monolayers (SAMs) to the redox-active heme unit of cytochrome c has enabled the electron-transfer mechanism to be studied as a function of distance. Comparison of the kinetic data for this system (see graph) with earlier data on COOH-terminated SAMs requires a change in the electron-transfer mechanism with distance from the electrode surface that does not involve large-amplitude conformational rearrangement.

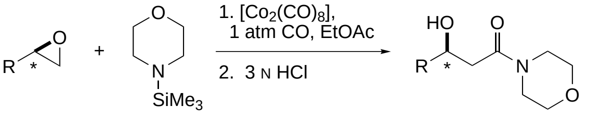


Angew. Chem. **2002**, *114*, 4894–4897

Keywords: bioorganic chemistry · cytochromes · electron transfer · proteins · self-assembly

---

Keeping the CO pressure down is a crucial, practical feature of the new methodology for the carbonylation of terminal epoxides. β-Hydroxy morpholinyl amides are generated directly in optically pure form [Eq. (1)], and these building blocks can be applied in a variety of acyl transfer reactions. A useful illustration is provided in the concise synthesis of δ-hydroxy-β-ketoesters, key intermediates for the preparation of the statin class of HMG-CoA reductase inhibitors.

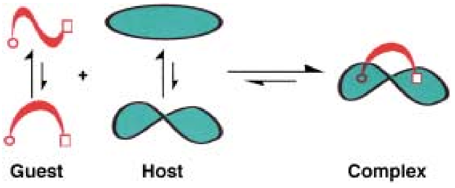


(1)

Angew. Chem. **2002**, *114*, 4897–4899

Keywords: amides · carbonylation · cobalt · epoxides · homogeneous catalysis

Adaptive systems: The conformationally flexible *p*-sulfonated calix[8]arene and photolabile cholinergic ligands adapt to each other and select the right conformers to form ditopic binding complexes (see schematic representation), thus mimicking ligand binding in biological receptors or enzymes.



Angew. Chem. **2002**, *114*, 4900–4902

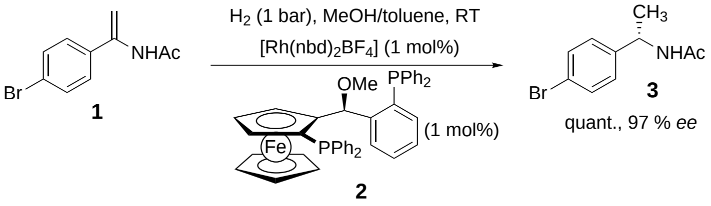
A. Specht, P. Bernard, M. Goeldner,*
L. Peng* 4706–4708

Mutually Induced Formation of Host–Guest Complexes between *p*-Sulfonated Calix[8]arene and Photolabile Cholinergic Ligands

Keywords: calixarenes · cholinergic ligands · host–guest systems · inclusion compounds · receptors

---

A new synthetic approach allows the synthesis of taniaphos-analogous ligands **2** with inverted α configuration $(S_\mathrm{p},\alpha S)$. This new class of ferrocenyl ligands displays excellent enantioselectivity and enhanced reactivity in several types of asymmetric hydrogenation reactions (e.g. **1**→**3**).



Angew. Chem. **2002**, *114*, 4902–4905

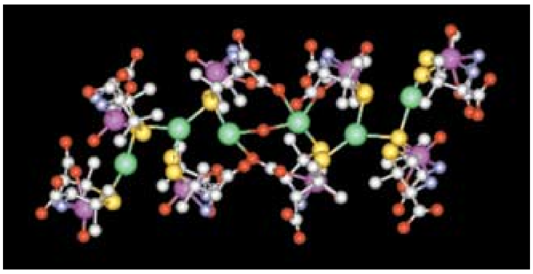
M. Lotz, K. Polborn,
P. Knochel* 4708–4711

New Ferrocenyl Ligands with Broad Applications in Asymmetric Catalysis

Keywords: asymmetric synthesis · ferrocenyl ligands · homogeneous catalysis · hydrogenation · P ligands

---

Re^{V} polymer/oligomer switching: The aggregation of Re^{V} octahedra, [ReO(D-pen-N,O)(D-pen-N,O,S)]$^-$ (D-$\mathrm{H_2}$pen = D-penicillamine), assisted by Ag^{I} ions, leads to the formation of a 2D $(\mathrm{Re}^{\mathrm{V}}_2\mathrm{Ag}^{\mathrm{I}}_2)_n$ coordination polymer **1**, which is converted into a $\mathrm{Re}^{\mathrm{V}}_8\mathrm{Ag}^{\mathrm{I}}_6$ coordination oligomer **2** (see picture; Ag green, S yellow, Re purple, O red, N blue). While **1** results from the self-assembly of $\mathrm{Re}^{\mathrm{V}}_2\mathrm{Ag}^{\mathrm{I}}_2$ units through Ag–O coordination bonding, the self-assembly of $\mathrm{Re}^{\mathrm{V}}_8\mathrm{Ag}^{\mathrm{I}}_6$ molecules in **2** is through COOH⋯OOC hydrogen bonding.



Angew. Chem. **2002**, *114*, 4905–4909

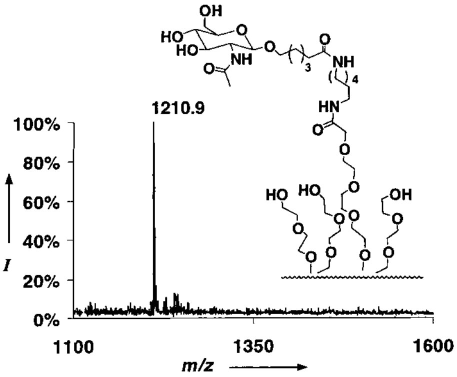
T. Konno,* Y. Shimazaki, T. Yamaguchi,
T. Ito, M. Hirotsu 4711–4715

A Remarkable 14-Nuclear $\mathrm{Re}^{\mathrm{V}}_8\mathrm{Ag}^{\mathrm{I}}_6$ Coordination Oligomer Derived from a 2D $(\mathrm{Re}^{\mathrm{V}}_2\mathrm{Ag}^{\mathrm{I}}_2)_n$ Coordination Polymer with D-Penicillaminate

Keywords: aggregation · rhenium · S ligands · silver · supramolecular chemistry

---

Peptide and carbohydrate biochips can be assayed with MALDI mass spectrometry. Self-assembled monolayers (SAMs) that are modified with ligands provide a platform for identifying selective protein–ligand and enzyme–substrate interactions. MALDI provides a rapid and sensitive method for detection and avoids the need to label protein analytes with fluorescent or radioactive tags. The picture shows the mass spectrum of a SAM presenting a carbohydrate.



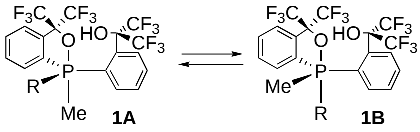
Angew. Chem. **2002**, *114*, 4909–4912

J. Su, M. Mrksich* 4715–4718

Using Mass Spectrometry to Characterize Self-Assembled Monolayers Presenting Peptides, Proteins, and Carbohydrates

Keywords: biochips · carbohydrates · glycosylation · mass spectrometry · monolayers

Position of importance: The relative apicophilicity of two substituents linked by a carbon atom to a pentacoordinate phosphorus center such as that in compounds **1** was determined based on the equilibrium ratio of pseudorotamers (**1A** and **1B**) in solution. A distinct solvent effect on the relative apicophilicity and a novel phenomenon in which two different pseudorotamers cocrystallized in the same single crystal were observed.



R: Et, *n*Pr, *n*Bu, CH_2OMe, Ph, $CH_2C_6H_4$(*p*-Me), CH_2Ph, $CH_2C_6H_4$(*p*-F)

Angew. Chem. **2002**, *114*, 4912–4916

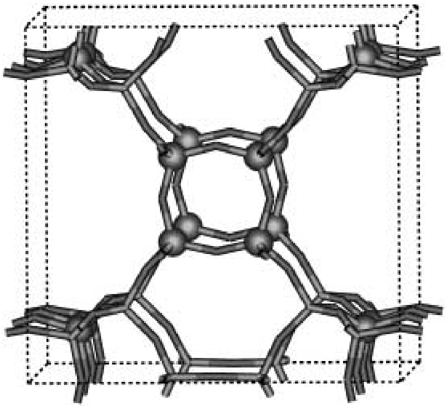
S. Matsukawa, K. Kajiyama, S. Kojima, S.-y. Furuta, Y. Yamamoto, K.-y. Akiba* 4718–4722

A Method for Determining the Difference in Relative Apicophilicity of Carbon-Containing Substituents of 10-P-5 Phosphoranes

Keywords: apicophilicity • hypervalent compounds • phosphorus • solvent effects • structure elucidation

---

Ge-directed zeolites. Forcefield atomic simulations are used to investigate the location of the Ge atoms and the structure-directing agents (SDAs) in the Ge containing ITQ-17 zeolite (see picture). The Ge atoms are found to locate preferentially at the T1 sites which form double four-ring (D4R) units. A combined theoretical and experimental treatment has allowed us to prove the preferential location of Ge atoms in the double four-member rings of the polymorph C of Beta zeolite, and its corresponding structure-directing effect to be demonstrated.



Angew. Chem. **2002**, *114*, 4916–4920

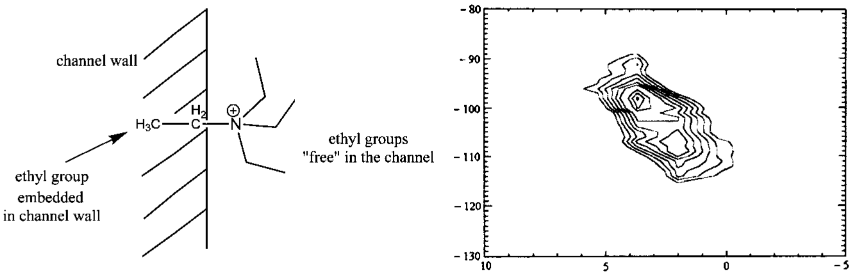
G. Sastre, J. A. Vidal-Moya, T. Blasco, J. Rius, J. L. Jordá, M. T. Navarro, F. Rey, A. Corma* 4722–4726

Preferential Location of Ge Atoms in Polymorph C of Beta Zeolite (ITQ-17) and Their Structure-Directing Effect: A Computational, XRD, and NMR Spectroscopic Study

Keywords: germanium • polymorphism • silicates • structure elucidation • zeolites

---

New insight into the binding modes of bimetallic clusters and catalytically active nanoparticles to the mesoporous solid MCM-41 has been obtained from solid-state NMR spectroscopic data (see figure, right). From this study, a model has been proposed to explain the interactions between the pore walls and the cluster. It has been shown that the counterion plays an important role in the anchoring process (see figure, left).



Angew. Chem. **2002**, *114*, 4920–4923

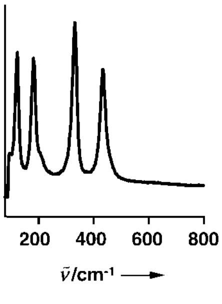
M. D. Jones, M. J. Duer,* S. Hermans, Y. Z. Khimyak, B. F. G. Johnson, J. M. Thomas 4726–4729

Solid-State NMR Studies of MCM-41 Supported with a Highly Catalytically Active Cluster

Keywords: bimetallic clusters • heterogeneous catalysis • mesoporous materials • NMR spectroscopy

---

Getting all steamed up: The active phase formed in situ in the catalytic hydrolysis of chlorinated compounds, such as CCl_4, at relatively low temperatures consists of a lanthanide oxide chloride, as evident from vibrational frequencies at 125, 188, 215, 335, and 440 cm^{-1} in the Raman spectrum (see picture). This active phase remains stable as long as steam is provided, and produces CO_2 and HCl as the only reaction products.



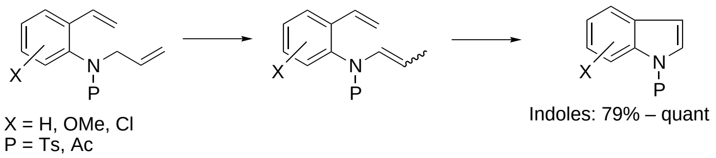
Angew. Chem. **2002**, *114*, 4924–4926

P. Van der Avert, B. M. Weckhuysen* 4730–4732

Low-Temperature Destruction of Chlorinated Hydrocarbons over Lanthanide Oxide Based Catalysts

Keywords: chlorinated hydrocarbons • heterogeneous catalysis • lanthanides • Raman spectroscopy

A ruthenium complex, generated from the Grubbs carbene catalyst with vinyloxytrimethylsilane, catalyzed the isomerization of terminal alkenes $RCH_2{-}CH{=}CH_2$ to internal alkenes $RCH{=}CH{-}CH_3$. Application of this olefin isomerization to 2-(*N*-allylamino)styrene gave the corresponding enamines, which were converted into indoles by a standard ring-closing metathesis, see scheme (Ts = tosyl).



Angew. Chem. **2002**, *114*, 4926 – 4928

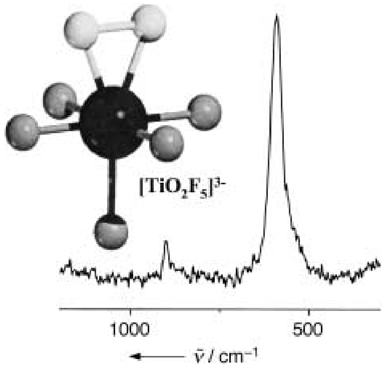
M. Arisawa, Y. Terada, M. Nakagawa,
A. Nishida* .... 4732 – 4734

Selective Isomerization of a Terminal Olefin Catalyzed by a Ruthenium Complex: The Synthesis of Indoles through Ring-Closing Metathesis

Keywords: heterocycles • isomerization • metathesis • ring closure • vinyls

---

The characteristic yellow color of the TS-1/H_2O_2/H_2O system is attributed to a "side-on" Ti – peroxo species, presumed to be the active intermediate in partial oxidation reactions. Resonance Raman spectroscopic analysis of both the zeolite system and a model salt ($(NH_4^+)_3(TiO_2F_5)^{3-}$, see picture) are combined with the analysis of a Ti-free silicalite to prove the structure of the hitherto unknown species.



Angew. Chem. **2002**, *114*, 4928 – 4931

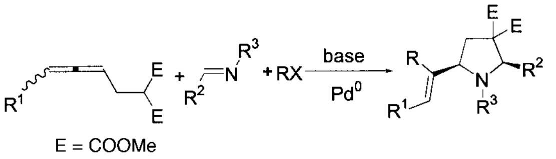
S. Bordiga,* A. Damin, F. Bonino,
G. Ricchiardi, C. Lamberti,
A. Zecchina .... 4734 – 4737

The Structure of the Peroxo Species in the TS-1 Catalyst as Investigated by Resonant Raman Spectroscopy

Keywords: charge transfer • peroxides • Raman spectroscopy • titanium • zeolites

---

***cis*-2,5-Disubstituted pyrrolidine skeletons** have been constructed by the Pd^0-catalyzed three-component tandem double-addition – cyclization reaction of 2-(2,3-butadienyl)malonates, organohalides, and imines (see scheme, yields: 81 – 100 %; *cis*/*trans* >95:5).



Angew. Chem. **2002**, *114*, 4931 – 4934

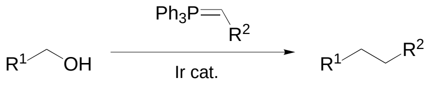
S. Ma,* N. Jiao .... 4737 – 4740

Pd^0-Catalyzed Three-Component Tandem Double-Addition – Cyclization Reaction: Stereoselective Synthesis of *cis*-Pyrrolidine Derivatives

Keywords: allenes • cyclization • diastereoselectivity • palladium • solvent effects

---

Hydrogen atoms are borrowed during the in situ oxidation of the starting alcohol to the corresponding aldehyde and are subsequently returned in the hydrogenation of the alkene intermediate, which is formed by Wittig olefination of the aldehyde. This process permits an indirect Wittig reaction of alcohols without overall oxidation and offers an alternative to traditional methods that involve, for example, conversion of an alcohol into an alkyl halide.



Angew. Chem. **2002**, *114*, 4934 – 4937

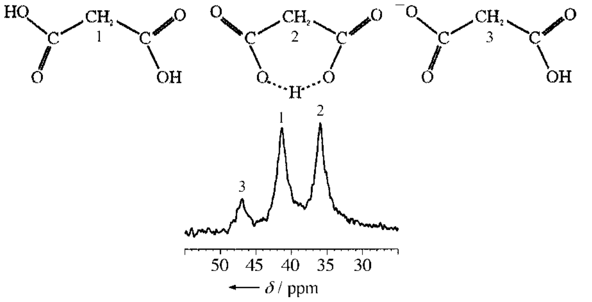
M. G. Edwards,
J. M. J. Williams* .... 4740 – 4743

Catalytic Electronic Activation: Indirect "Wittig" Reaction of Alcohols

Keywords: alcohols • homogeneous catalysis • iridium • transfer hydrogenation • wittig reactions

1433-7851/02/4124-4605 $ 20.00+.50/0

Information about the presence and the nature of various deprotonated forms of malonic acid in lyophilizates prepared from parent solutions at different pH values can be obtained by solid-state, natural abundance ^{13}C NMR spectroscopy, particularly if a ^{13}C-enriched substrate is used (see picture). p*K* values calculated from solid-state acid:base ratios are found to be equal to those classically measured in the liquid state.



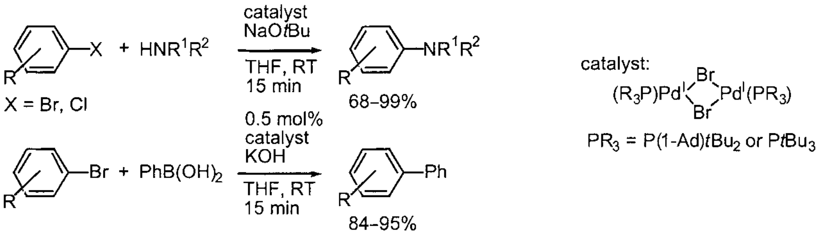
Angew. Chem. **2002**, *114*, 4937–4939

R. Colsenet, C. Gardiennet, B. Henry,
P. Tekely* 4743–4745

A Straightforward Detection of Deprotonated Conformers of Malonic Acid by Solid-State ^{13}C NMR Spectroscopy

Keywords: basicity • carboxylic acids • hydrogen bonds • NMR spectroscopy

Exceptionally fast oxidative addition of an aryl chloride (or a deactivated aryl bromide) to the active Pd^0 center, which is ligated by sterically demanding phosphanes, occurs during coupling reactions catalyzed by air-stable Pd^I dimers as shown in the scheme. As a result, the reactions of aryl chlorides and bromides with amines and boronic acids at room temperature are complete within a few minutes. 1-Ad = 1-adamantyl.



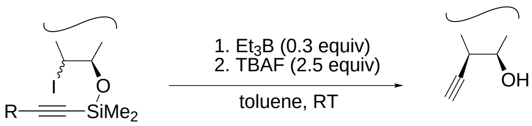
Angew. Chem. **2002**, *114*, 4940–4942

J. P. Stambuli, R. Kuwano,
J. F. Hartwig* 4746–4748

Unparalleled Rates for the Activation of Aryl Chlorides and Bromides: Coupling with Amines and Boronic Acids in Minutes at Room Temperature

Keywords: amination • aryl chlorides • C–C coupling • oxidative addition • palladium

Atom-transfer 5-*exo* cyclization and subsequent elimination occur when ethynyldimethylsilyl ethers of iodohydrins are treated with Et_3B followed by tetrabutylammonium fluoride (TBAF) to give the corresponding *cis*-configured α-hydroxy ethynyl compounds in high yield (see scheme). This is the first example of the use of a radical reaction to introduce an ethynyl group.



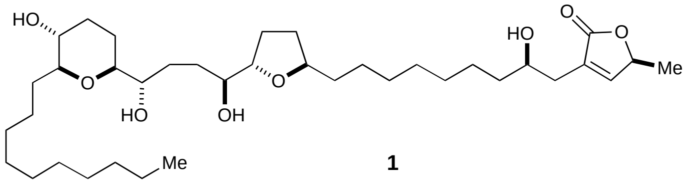
Angew. Chem. **2002**, *114*, 4942–4945

M. Sukeda, S. Ichikawa, A. Matsuda,
S. Shuto* 4748–4750

A New Entry to the Stereoselective Introduction of an Ethynyl Group by a Radical Reaction: Synthesis of the Potential Antimetabolite 2′-Deoxy-2′-*C*-ethynyluridine

Keywords: alkynes • C–C coupling • elimination • nucleosides • radical reactions

The THP and THF rings which are regarded as the characteristic structural features of mucocin (**1**) were constructed by a SmI_2-induced reductive cyclization of β-alkoxy acrylate and oxidative cyclization of a homoallyl alcohol, respectively. The key intermediates were synthesized through an efficient desymmetrization of a C_2-symmetric tetraol.



1

Angew. Chem. **2002**, *114*, 4945–4948

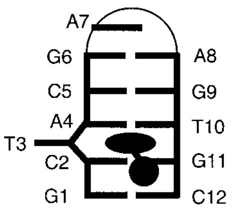
S. Takahashi,* A. Kubota,
T. Nakata* 4751–4754

Stereoselective Total Synthesis of Mucocin, an Antitumor Agent

Keywords: antitumor agents • cyclization • natural products • samarium • total synthesis

A bulged conformation in which the T3 base is flipped-out of the helical stack of the novel DNA hairpin **H2** allowing complementary pairing downstream of the intercalation site (see picture) is stabilized by binding of the drug nogalamycin. This finding was readily confirmed by detailed analysis of the chemical shift and NOE data.

Angew. Chem. **2002**, *114*, 4948–4951



H2

M. L. Colgrave, H. E. L. Williams,
M. S. Searle* 4754–4756

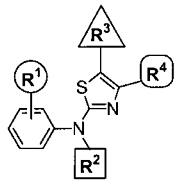
Structure of a Drug-Induced DNA T-Bulge: Implications for DNA Frameshift Mutations

Keywords: DNA recognition · DNA structures · molecular dynamics · NMR spectroscopy · noncovalent interactions

---

A 10-step (!) solid-phase synthesis employing the traceless hydrazide linker provides efficient access to a 2-aminothiazole library (see scheme) that yielded access to a new class of tyrosine kinase inhibitors with dual selectivity for the vascular endothelial growth factor receptor VEGFR-2 and the Tie-2 receptor tyrosine kinases.

Angew. Chem. **2002**, *114*, 4951–4955



F. Stieber, R. Mazitschek, N. Soric,
A. Giannis,* H. Waldmann* 4757–4761

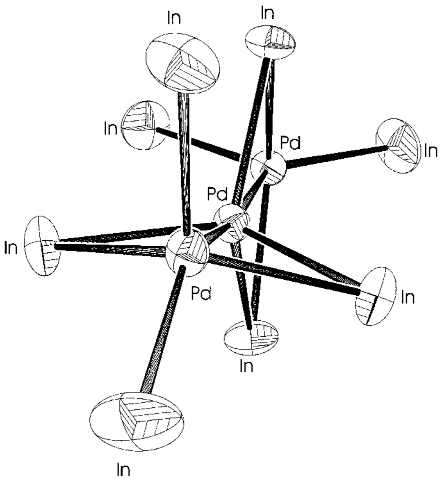
Traceless Solid-Phase Synthesis of 2-Aminothiazoles: Receptor Tyrosine Kinase Inhibitors with Dual Selectivity for Tie-2 and VEGFR-2

Keywords: combinatorial chemistry · heterocycles · inhibitors · solid-phase synthesis

---

There is still much to discover: The assumption that monovalent Group 13 organometallic compounds exhibit a high potential as ligands in organometallic chemistry beyond their analogy to CO is confirmed by the synthesis of the title compound **1**. Complex **1**, the structure of which is unique and has no analogue in carbonyl cluster chemistry, is prepared by reaction of [(tmeda)Pd(CH$_3$)$_2$] with [InCp*]. tmeda = *N,N,N′,N′*-tetramethylethylenediamine, Cp* = pentamethylcyclopentadienide.

Angew. Chem. **2002**, *114*, 4955–4957



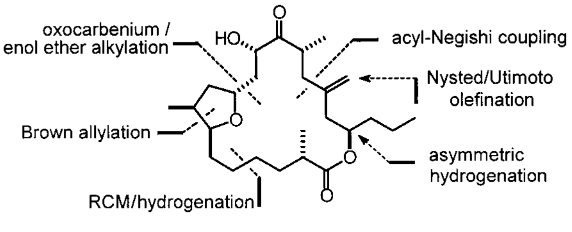
T. Steinke, C. Gemel, M. Winter,
R. A. Fischer* 4761–4763

[Pd$_3$(InCp*)$_4$(μ_2-InCp*)$_4$]: Three Linearly Arranged Palladium Atoms Wrapped into a Fluxional Shell of Eight InCp* Ligands

Keywords: cluster compounds · cyclopentadienyl ligands · Group 13 elements · indium · palladium

---

Organometallic chemistry in general and catalysis in particular are used in the first total synthesis of amphidinolide T4 (see scheme); a prototype member of a series of macrolide antibiotics of marine origin with rings containing an odd number of carbon atoms.



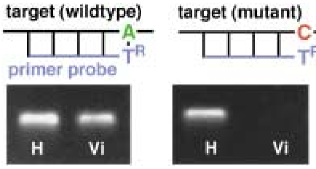
Angew. Chem. **2002**, *114*, 4958–4960

A. Fürstner,* C. Aïssa, R. Riveiros,
J. Ragot 4763–4766

Total Synthesis of Amphidinolide T4

Keywords: macrolides · metathesis · natural products · ruthenium · total synthesis · zinc

Increased selectivity in PCR! Robust systems that allow the direct detection of single nucleotide variations through PCR methods will be increasingly important for rapid comparative genome analysis or mutation detection. Primer probes bearing supplemental chemical modifications (R = vinyl) significantly increase the selectivity of PCR compared to unmodified probes (R = H), even when the target sequences differ in only one nucleotide (see picture).



Angew. Chem. **2002**, *114*, 4961–4963

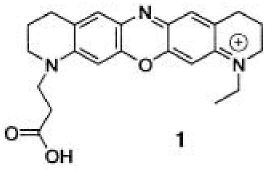
M. Strerath, A. Marx* 4766–4769

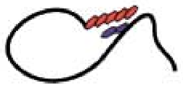
Tuning PCR Specificity by Chemically Modified Primer Probes

Keywords: DNA · mutations · oligonucleotides · polymerase chain reaction · polymerases

---

Single-molecule spectroscopy for cancer diagnostics: Short dye-labeled peptide epitopes derived from human p53 show strong fluorescence quenching owing to efficient electron transfer from a tryptophan residue to the fluorophore (**1**, see picture). The specific recognition of the peptide epitope by the antibody induces a change in the conformation which is accompanied by a strong increase in fluorescence intensity. The fluorescing antibody–peptide complex can be detected at the single-molecule level even in slightly diluted serum samples by using confocal fluorescence microscopy.


1



Angew. Chem. **2002**, *114*, 4964–4968

H. Neuweiler, A. Schulz, A. C. Vaiana, J. C. Smith, S. Kaul, J. Wolfrum, M. Sauer* 4769–4773

Detection of Individual p53-Autoantibodies by Using Quenched Peptide-Based Molecular Probes

Keywords: antibodies · fluorescent probes · hydrophobic effect · immunoassays · single-molecule studies

---

An excellent tool for gaining a better understanding of long-distance exchange interactions in complicated systems, such as the $S_2Y_Z^\bullet$ state of photosystem II, is provided by a relatively simple model for similar interactions between a dimanganese core and an organic radical in the complex $[(Me_4dtne)Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2CPhNIT)](ClO_4)_2$. Dual-mode EPR spectroscopy serves as an additional tool for determining the extent of these long-distance dipolar coupling interactions. Me_4dtne = 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane; HO_2CPhNIT = 2-(4-carboxyphenyl)-4,4,5,5-tetramethyl-3-oxyimidazolidin-1-oxide.

Angew. Chem. **2002**, *114*, 4969–4973

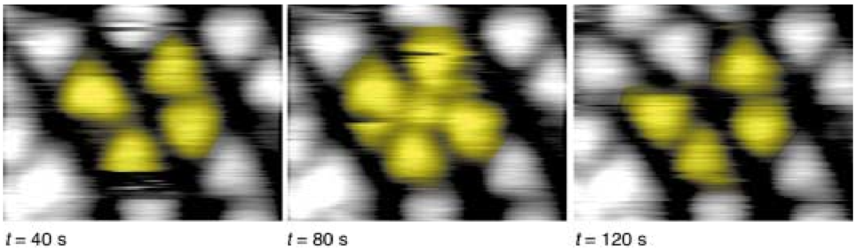
D. S. Marlin,* E. Bill,* T. Weyhermüller, E. Rentschler, K. Wieghardt* 4775–4779

Long-Distance Magnetic Interaction between a $Mn^{III}Mn^{IV}$ (S = 1/2) Core and an Organic Radical: A Spectroscopic Model for the $S_2Y_Z^\bullet$ State of Photosystem II

Keywords: EPR spectroscopy · magnetic properties · manganese · photosystem II · radicals

---

Reaction sequences under the microscope: Scanning tunneling microscopy has been used to follow the association and dissociation of the cloverleaf-shaped complex from 1,3,5-benzenetricarboxylic acid and Cu atoms from a metal surface one molecule at a time (see images). The lifetime of the complexes depends crucially on their local chemical enviroment.


t = 40 s t = 80 s t = 120 s

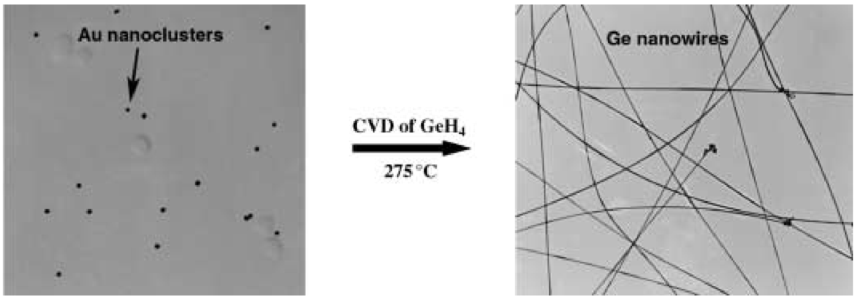
Angew. Chem. **2002**, *114*, 4973–4977

N. Lin,* A. Dmitriev, J. Weckesser, J. V. Barth,* K. Kern* 4779–4783

Real-Time Single-Molecule Imaging of the Formation and Dynamics of Coordination Compounds

Keywords: reaction dynamics · scanning probe microscopy · self-assembly · single-molecule studies · surface chemistry

Live-wire potential: Low-temperature growth of Ge nanowires has been achieved by the chemical vapor deposition of GeH_4 onto a SiO_2 substrate coated with Au nanoparticles (see picture). This technique, which represents the mildest growth conditions for single-crystal nanowire synthesis, can also be used for patterned growth processes. Under such conditions, the growth of high-quality nanowires on a variety of substrates is possible, which may yield many possibilities in nanotechnological applications.



Angew. Chem. **2002**, *114*, 4977–4980

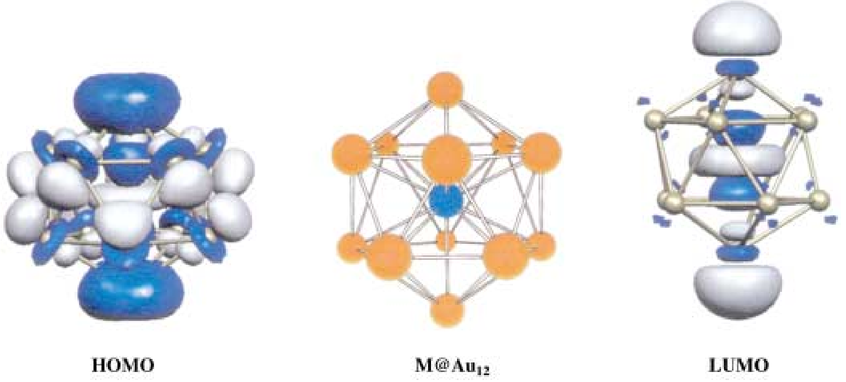
D. Wang, H. Dai* 4783–4786

Low-Temperature Synthesis of Single-Crystal Germanium Nanowires by Chemical Vapor Deposition

Keywords: chemical vapor deposition · germanium · nanotechnology · nanowires · patterned growth

---

Yes, W@Au$_{12}$ is icosahedral! We provide experimental verification of the recently proposed new class of gold clusters. Anion photoelectron spectroscopy and relativistic density functional calculations were used to show that both W@Au$_{12}$ and Mo@Au$_{12}$ are highly stable icosahedral clusters with large HOMO–LUMO gaps. The HOMO and LUMO of the I_h M@Au$_{12}$ clusters, both of h_g symmetry, are bonding and antibonding orbitals between the W(Mo) 5d(4d) and the Au 6s–5d$_{Z^2}$ hybrids oriented along the radial directions of the icosahedron, similar to the C 2s–2p$_z$ radial hybrids in C_{60}.



Angew. Chem. **2002**, *114*, 4980–4983

X. Li, B. Kiran, J. Li, H.-J. Zhai,
L.-S. Wang* 4786–4789

Experimental Observation and Confirmation of Icosahedral W@Au$_{12}$ and Mo@Au$_{12}$ Molecules

Keywords: cluster compounds · density functional calculations · gold · photoelectron spectroscopy · tungsten

---

It's a small world! The hydrothermal synthesis of a family of lanthanide hydroxide single-crystal nanowires has been achieved (see picture), the properties and dimensions of which can be tailored by changes in chemical potential and the pH value of the reaction media. Such materials might serve as templates for biological labeling agents, as one of many potential applications.

Angew. Chem. **2002**, *114*, 4984–4987

X. Wang, Y. Li* 4790–4793

Synthesis and Characterization of Lanthanide Hydroxide Single-Crystal Nanowires

Keywords: electron microscopy · hydrothermal synthesis · lanthanides · nanostructures

---

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

Accelerated publications

* Author to whom correspondence should be addressed

1433-7851/02/4124-4609 $ 20.00+.50/0

BOOKS

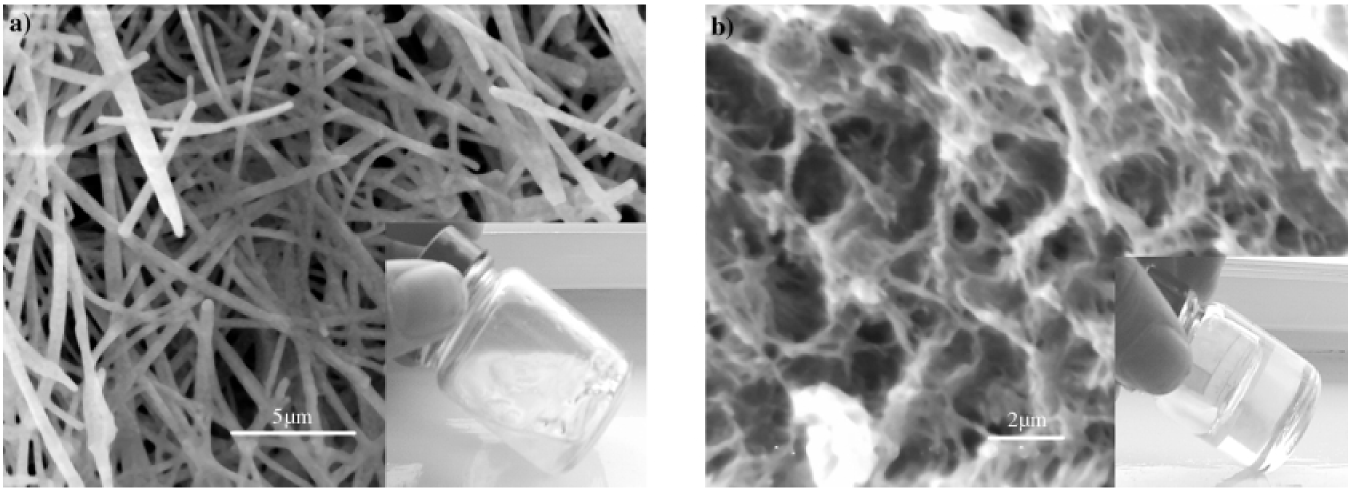
WEB SITES

SERVICE

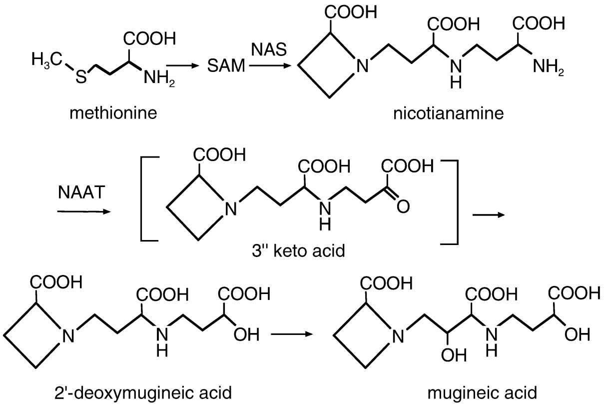
Don't forget all the Tables of Contents from 1998 onwards may be still found on the WWW under: http://www.angewandte.org

CORRIGENDUM

In the Communication by **X. Y. Liu** and **P. D. Sawant** in Issue 19, **2002**, pp. 3641–3645, the improved pictures shown below should have been used for Figure 1. For Figures 2 and 3, EVA should read EVACP. Throughout the paper lanosterol should read L/DHL.

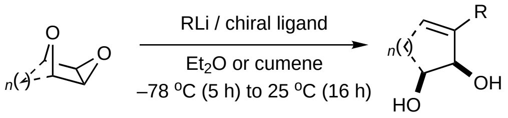


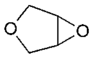
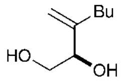
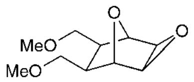
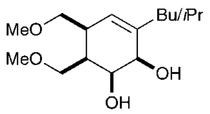
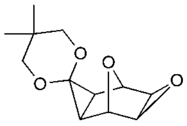
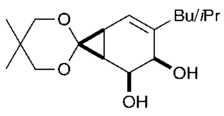
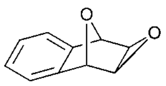
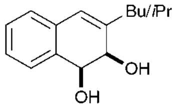
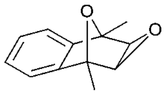
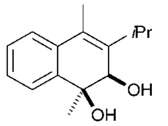
In the Minireview by **D. Staiger** in Issue 13, **2002**, pp. 2259–2264, Scheme 2 should be represented as follows:



In the Communication by **D. M. Hodgson** et al. in Issue 22, **2002**, pp. 4313–4316 errors were inadvertently introduced into Tables 1 and 2 during the printing. The correct sections of the tables are now given below. The editorial office apologizes for these errors.

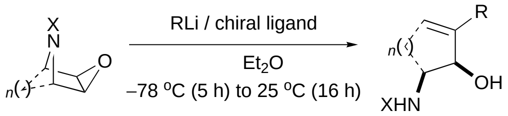
Table 1. Formation of enantioenriched diols.

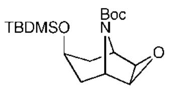
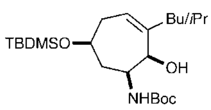
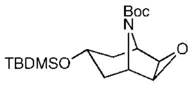
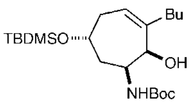
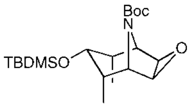
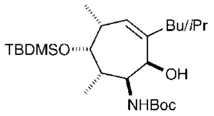
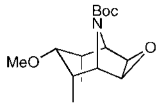
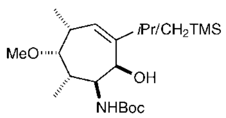


Entry[a]	Epoxide	RLi/ligand	Product[b]	Yield [%][c]	*ee* [%][d]
1		*n*BuLi/**1**		16	43
2		*n*BuLi/**2**		44	−42
3		*n*BuLi/**1**		46	34
4		*n*BuLi/**2**		34	−40
5		*i*PrLi/**1**		34	63
6		*n*BuLi/**1**		57	27
7		*i*PrLi/**1**		49	59
8		*n*BuLi/**1**		50	51
9		*i*PrLi/**1**		44	74
10		*i*PrLi/**1**		42	56

[a] Entries 1–10 carried out in Et_2O; entries 11–13 carried out in cumene. [b] Absolute configuration of predominant enantiomer obtained with (−)-sparteine (**1**) is shown (assigned by analogy with the sense of asymmetric induction in deprotonations of other *meso*-epoxides).[3] Bisoxazoline **2** preferentially produced the opposite configuration. [c] Yield of isolated product. [d] Determined by HPLC on a chiral stationary phase. TBDMS = *tert*-butyldimethylsilyl.

Table 2. Formation of enantioenriched amino alcohols.



Entry[a]	Epoxide	RLi/ligand	Product[b]	Yield [%][c]	*ee* [%][d]
9		*n*BuLi/**1**		83	41
10		*n*BuLi/**2**		60	−67
11		*i*PrLi/**1**		59	65
12		*n*BuLi/**1**		68	79
13		*n*BuLi/**1**		84	66
14		*n*BuLi/**2**		71	−67
15		*i*PrLi/**1**		85	71
16		*i*PrLi/**2**		72	−75
17		*i*PrLi/**1**		69	82
18		$TMSCH_2Li$/**1**		61	57
19		mixed[e]/**1**		66[f]	64

[a] Quenched at 25 °C, apart from entries 9–11 and 18, 19 (−5 °C), entry 12 (−78 °C), entries 13–16 (−30 °C), and entry 17 (−50 °C). [b] See Table 1 footnote [b]. [c] Yield of isolated product. [d] Determined by HPLC or GC on a chiral stationary phase. [e] *i*PrLi (1.1 equiv) and $TMSCH_2Li$ (2.5 equiv). [f] Allylsilane major product, 7 % of *i*Pr incorporation additionally observed. TMS = trimethylsilyl.

In the Communication of **F. E. Romesberg** and **P. G. Schultz** et al. in Issue 20, **2002**, p. 3841–3844, the authors should be given in the following order: Chengzhi Yu, Allison A. Henry, Peter G. Schultz,* and Floyd E. Romesberg*.

In the Communication by **K. Kim** et al. in Issue 23, **2002**, pp. 4474 – 4476, the permanent address for Professor Parimal K. Bharadwaj was unfortunately removed during editing. The editorial office apologizes for this error. His permanent address is:

Department of Chemistry
Indian Institute of Technology
Kanpure 208016 (India).

APOLOGY

In the Communication "Synthesis of Amphiphilic Conjugated Diblock Oligomers as Molecular Diodes" by **L. Yu** and **M.-K. Ng** (*Angew. Chem.* **2002**, *114*, 3750 – 3753; *Angew. Chem. Int. Ed.***2002**, *41*, 3598 – 3601) the authors missed a cross-reference to their thematically related but independent communication "Molecular Diodes Based on Conjugated Diblock Co-oligomers" (M.-K. Ng, D.-C. Lee, L. Yu, *J. Am. Chem. Soc.* **2002**, *124*(40), 11862 – 11863) and vice versa. The authors apologize for this oversight.