ANGEWANDTE
CHEMIE
INTERNATIONAL EDITION

A Journal of the
Gesellschaft
Deutscher Chemiker

2002
41/18
Pages 3297 – 3508

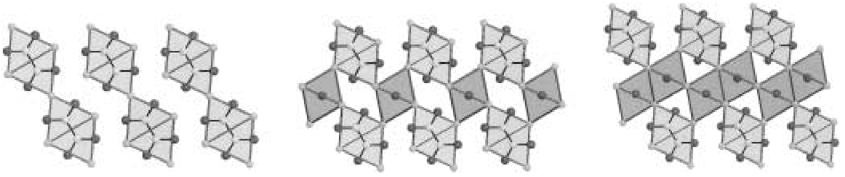
COVER PICTURE

The cover picture shows the newest member of an "elite" club of aromatic molecules. The platinabenzene, in which a benzene methine (CH) unit has been replaced by an isoelectronic platinum fragment, completes the series of metalla-aromatics containing third row, Group VIII metals (Os, Ir, Pt). Previously excluded, the molecule gains admittance to this select club because it exhibits properties similar to other six-membered ring heteroaromatic compounds (e.g., pyridine), such as ring planarity, delocalized bonding, and downfield shifts in the ^{1}H NMR spectrum. The platinabenzene shares a feature unique for the third period transition metals in that it requires no further stabilization by coordination to an additional metal center. More on the structure and properties of this molecule can be found in the communication by Haley et al. on p. 3470 ff.

REVIEWS

Contents

Between molecular and solid-state chemistry: the nitridoborates of the lanthanides form both saltlike and metal-rich compounds, and are synthesized through solid-state metathesis reactions with dinitridoborate ions. They contain ions such as $[BN]^{n-}$, $[BN_2]^{3-}$, $[B_2N_4]^{8-}$, $[B_3N_6]^{9-}$, and $[BN_3]^{6-}$. A characteristic structure principle can be derived for nitridoborates and their nitrides as shown in the picture for structures with B_2N_4 anions.



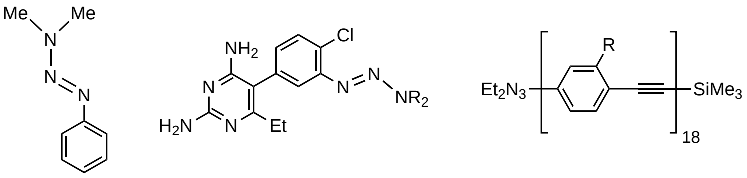
Angew. Chem. **2002**, *114*, 3468 – 3483

B. Blaschkowski, H. Jing,
H.-J. Meyer* .... 3322 – 3336

Nitridoborates of the Lanthanides: Synthesis, Structure Principles, and Properties of a New Class of Compounds

Keywords: borates · lanthanide · nitrides · nitridoborates · solid-state structures

Extraordinarily versatile best describes triazenes, a class of biologically and synthetically useful molecules (see picture). Triazenes exhibit several types of reactivity depending on the conditions used and can yield a wide variety of functional groups when treated with acids, bases, or iodomethane. Triazenes can form links to solid supports, simplify polymer or macrocycle synthesis, or act as anticancer agents, all of which are described in this review.



Angew. Chem. **2002**, *114*, 3484 – 3498

D. B. Kimball, M. M. Haley* 3338 – 3351

Triazenes: A Versatile Tool In Organic Synthesis

Keywords: cross-coupling · cyclization · heterocycles · protecting groups · solid-phase synthesis

ESSAY

Moral justification? How can we choose from the different moral view points, which is correct and which is inappropriate, when the supporters of each view point defend and justify their position which such vehemence. In other words is there a rational basis for norms?

Angew. Chem. **2002**, *114*, 3499 – 3505

G. Patzig* .... 3353 – 3358

Can Moral Norms be Rationally Justified?

Keywords: ethics · norms · philosophy of science

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.org

Hydroboration of Coordinated Dinitrogen: A New Reaction for the N_2 Ligand that Results in Its Functionalization and Cleavage	M. D. Fryzuk,* B. A. MacKay, S. A. Johnson, B. O. Patrick	◆
Protonated Benzene: IR Spectrum and Structure of $C_6H_7^+$	N. Solcà, O. Dopfer*	◆
Single-Step Assembly of a C_2-Symmetrical Palladium(IV) Spirocyclic Complex	Y. Yamamoto,* T. Ohno, K. Itoh	◆
Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide Based “Nanosponge”: En Route to Sphere-Surface and Nanoporous-Cluster Chemistry	A. Müller,* E. Krickemeyer, H. Bögge, M. Schmidtmann, S. Roy, A. Berkle	◆
Syntheses and Crystal Structures of the New Ag-S Clusters $[Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4(triphos)_4]$ and $[Ag_{188}S_{94}(PnPr_3)_{30}]$	X.-J. Wang, T. Langetepe, C. Persau, B.-S. Kang, D. Fenske*	
A Synthesis Route to Enantiomerically Pure Jasmonoids	M. Ernst, G. Helmchen*	
Ethane and Ethylidene Dicarboxylates from the Ruthenium(II)-Catalyzed Disproportionative Addition of Carboxylic Acids to Ethene	T. Funaioli,* F. Marchetti, G. Fachinetti*	
Cell-Free Biosynthesis of Fluoroacetate and 4-Fluorothreonine in *Streptomyces cattleya*	C. Schaffrath, S. L. Cobb, D. O’Hagan*	
Selective Measurements of a Nitroxide – Nitroxide Distance of 5 nm and a Nitroxide – Copper Distance of 2.5 nm in a Terpyridine-Based Copper(II) Complex by Pulse EPR Spectroscopy	E. Narr, A. Godt, G. Jeschke*	

1433-7851/02/4118-3300 $ 20.00+.50/0

HIGHLIGHTS

Without large investments in new clean-room facilities, the nano- and microstructures described here can be achieved by the combination of wet-chemistry with existing conventional lithographic techniques. One of the advantages of the method is that it allows the specific formation of aperiodic patterns, which are of specific interest, since the symmetry that is an intrinsic part of the self-assembly of molecules can be overridden. Another advantage is that the use of organic–inorganic templates allows access to pure inorganic nanostructures.

Angew. Chem. **2002**, *114*, 3507–3510

J. P. Spatz* 3359–3362

Nano- and Micropatterning by Inorganic Templating of Hierarchical Self-Assembled Structures

Keywords: imprinting · lithography · nanotechnology · surface chemistry

---

Moieties that can be cross-linked appear to be the necessary feature of dendrimers that can be used to make poled polymers displaying high chromophore density, excellent electrooptic properties, and good thermal and temporal stability. Such materials could find use in optical telecommunications and public networking.

Angew. Chem. **2002**, *114*, 3511–3514

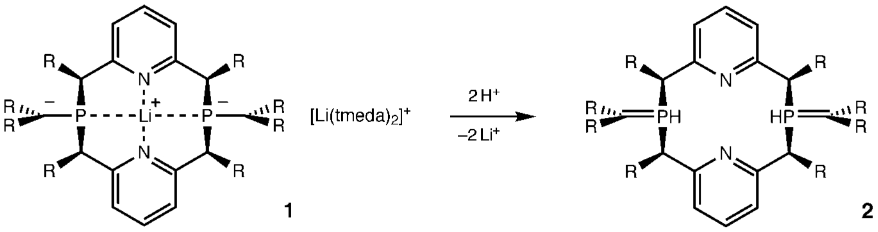
M. E. van der Boom* 3363–3366

Nanostructured Molecular Materials for Device-Quality, Highly Efficient Electrooptic Poled Polymers

Keywords: dendrimers · electrooptic properties · nonlinear optics · organic devices · thin films

COMMUNICATIONS

The thermodynamically less favorable PH-ylide **2**, not the corresponding phosphane, is formed in the kinetically controlled protonation of the cyclic phosphamethanide complex **1**. As the electrostatic potential on the surfaces of **1** shows, the attack of the proton on the sterically well shielded methanide carbon atom, and thus the formation of the phosphane form, is hindered. Consequently, a stable phosphonium ylide could be isolated for the first time in the condensed phase and characterized by X-ray crystallography. R = $SiMe_3$, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.



Angew. Chem. **2002**, *114*, 3515–3519

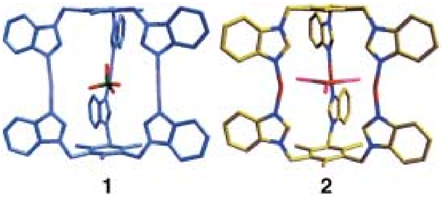
S. Ekici, D. Gudat, M. Nieger,
L. Nyulaszi,* E. Niecke* 3367–3371

Kinetically Controlled Protonation of a Cyclic Phosphamethanide Complex to a PH-Phosphonium Ylide

Keywords: macrocyclic ligands · P ligands · substituent effects · tautomerism · ylides

---

Thermodynamically stable, but kinetically labile: Trigonal-prismatic M_3L_2 metallocages occur in $[BF_4 \subset \{Ag_3(MsTBim)_2\}](BF_4)_2$ (**1**) and $[\{CuI_3 \subset [Cu_3(MsTBim)_2]\}_2](Cu_2I_4)$ (**2**), the latter with an unprecedented metal-complex-host/metal-complex-guest arrangement. Large anions such as $CF_3SO_3^-$ or BPh_4^- have to reside outside the cage facing its “windows”. MsTBim = 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene.



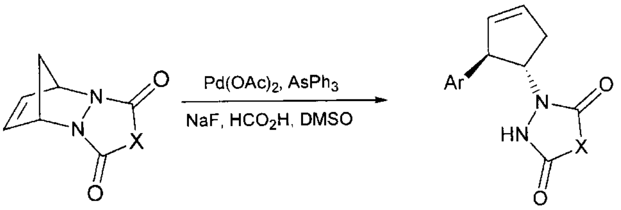
Angew. Chem. **2002**, *114*, 3519–3523

C.-Y. Su, Y.-P. Cai, C.-L. Chen, F. Lissner,
B.-S. Kang,* W. Kaim* 3371–3375

Self-Assembly of Trigonal-Prismatic Metallocages Encapsulating BF_4^- or CuI_3^{2-} as Anionic Guests: Structures and Mechanism of Formation

Keywords: cage compounds · copper · host–guest systems · self-assembly · solid-state structures

The product of a formal hydrazidoarylation of cyclopentadiene was obtained for the first time by palladium-catalyzed reaction of diaza[2.2.1]bicyclic alkenes with aryl halides in the presence of triphenylarsane, sodium fluoride, and formic acid under stereoselective cleavage of a C–N bond (see scheme).



Angew. Chem. **2002**, *114*, 3523–3526

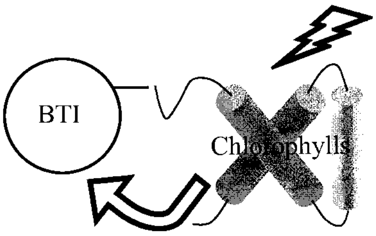
M.-L. Yao, G. Adiwidjaja,
D. E. Kaufmann* 3375–3378

Two-Step, Stereoselective Hydrazidoarylation of 1,3-Cyclopentadiene

Keywords: As ligands • fluoride • hydrazide • hydroarylation • palladium

---

A simple model of a plant photosystem has been constructed from a recombinant light-harvesting chlorophyll *a/b* protein (LHCIIb) of the plant photosynthetic apparatus and a covalently coupled benzoylterrylene-3,4-dicarboximide dye (BTI) as an artificial energy trap (see picture). Up to 85% of the energy absorbed by LHCIIb are transferred to the acceptor.



Angew. Chem. **2002**, *114*, 3526–3529

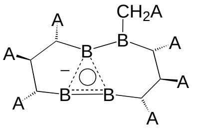
H. Wolf-Klein, C. Kohl, K. Müllen,
H. Paulsen* 3378–3380

Biomimetic Model of a Plant Photosystem Consisting of a Recombinant Light-Harvesting Complex and a Terrylene Dye

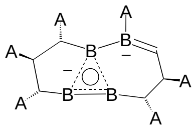
Keywords: chlorophyll • fluorescence spectroscopy • membrane proteins • photosynthesis • polycycles

---

One extremely short and two relatively long B–B bonds are found for the B_3 ring of compounds **1** and **2**. This characteristic of three-membered, two-electron double aromatic compounds was predicted as early as 1994 and has now been experimentally realized for the first time. A = $SiMe_3$.



1



2

Angew. Chem. **2002**, *114*, 3529–3531

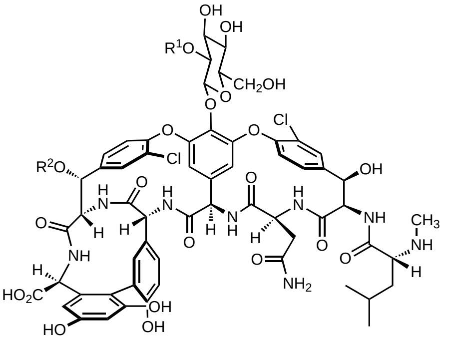
C. Präsang, A. Mlodzianowska, Y. Sahin, M. Hofmann, G. Geiseler, W. Massa,
A. Berndt* 3380–3382

Triboracyclopropanates: Two-Electron Double Aromatic Compounds with Very Short B–B Distances

Keywords: aromaticity • boron • density functional calculations • multicentered bonds

---

Mutasynthesis—a very potent tool? The two chlorine atoms attached to the aglycon of vancomycin-type glycopeptide antibiotics (see structure) have considerable influence on the antibiotic activity of each compound. By combining molecular genetic methods and chemical synthesis these chlorine atoms can be replaced by fluorine atoms. The described approach may also be applicable to modifying other parts of the glycopeptide molecule.



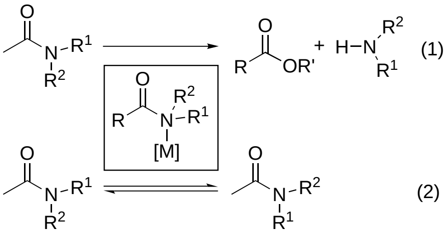
Angew. Chem. **2002**, *114*, 3531–3534

S. Weist, B. Bister, O. Puk, D. Bischoff, S. Pelzer, G. J. Nicholson, W. Wohlleben,
G. Jung, R. D. Süssmuth* ... 3383–3385

Fluorobalhimycin—A New Chapter in Glycopeptide Antibiotic Research

Keywords: antibiotics • balhimycin • glycopeptides • mutasynthesis • structure elucidation

Unusual coordination compounds: It has long been postulated that well-known and important reactions of tertiary amides such as C-N cleavage [Eq. (1)] and *cis–trans* isomerization [Eq. (2)] may proceed via nitrogen-coordinated metal complexes. We report the first evidence for a well-defined structure-function relationship in these unusual compounds.



Angew. Chem. **2002**, *114*, 3535–3537

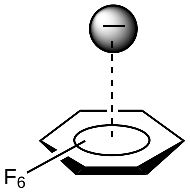
N. Niklas, F. W. Heinemann, F. Hampel, R. Alsfasser* 3386–3388

Activation of the Tertiary Carboxamide C–N Bond in Werner Complexes: A Classical Structure–Function Relationship

Keywords: amides · cadmium · cleavage reactions · coordination chemistry · copper · isomerization

---

Hovering above the π-electron cloud, an anion positioned over hexafluorobenzene along the C_6 axis as shown here interacts with the permanent quadrupole of the arene. Crystallographic and computational evidence demonstrate that anion–π interactions exist and are energetically favorable.



Angew. Chem. **2002**, *114*, 3539–3542

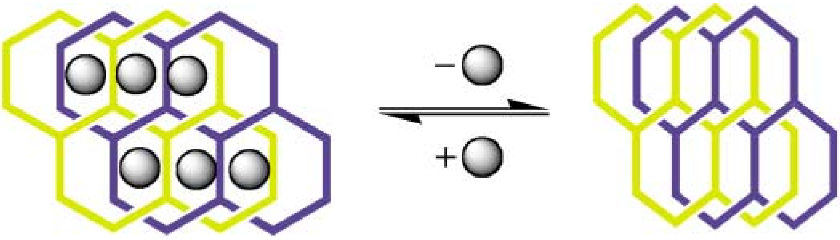
D. Quiñonero, C. Garau, C. Rotger, A. Frontera,* P. Ballester, A. Costa, P. M. Deyà* 3389–3392

Anion–π Interactions: Do They Exist?

Keywords: ab initio calculations · anions · noncovalent interactions · pi interactions

---

Double interpenetration: Guest molecules can control the formation of an unprecedented interlinked network consisting of zinc and a 3D tridentate ligand. The network shrinks when guest molecules are removed and swells when they are returned (see scheme).



Angew. Chem. **2002**, *114*, 3542–3545

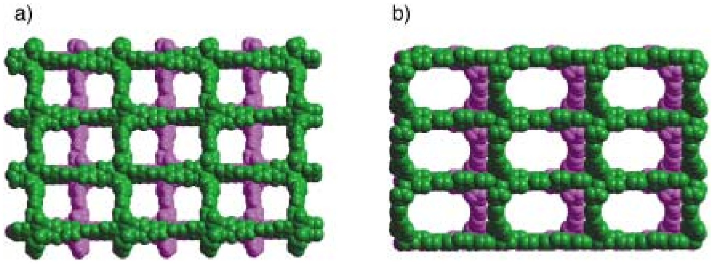
K. Biradha, M. Fujita* 3392–3395

A Springlike 3D-Coordination Network That Shrinks or Swells in a Crystal-to-Crystal Manner upon Guest Removal or Readsorption

Keywords: host-guest systems · solid-state structures · X-ray diffraction · zeolite analogues · zinc

---

Changing channels! The crystal-to-crystal sliding of a 2D network between two packing modes is triggered by the guest exchange of solvent molecules, and results in considerable difference in the channel dimensions (a → b; see scheme).



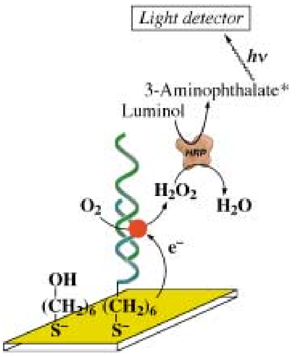
Angew. Chem. **2002**, *114*, 3545–3548

K. Biradha, Y. Hongo, M. Fujita* 3395–3398

Crystal-to-Crystal Sliding of 2D Coordination Layers Triggered by Guest Exchange

Keywords: host-guest systems · nickel · solid-state structures · X-ray diffraction · zeolite analogues

Making light work for DNA detection: Amplified DNA detection is accomplished by doxorubicin intercalated into double-stranded DNA assembled on Au-electrodes. Stimulated electrogenerated biochemiluminescence or biocatalyzed precipitation of an insoluble product amplify the DNA sensing that is being transduced by light emission (see picture; HRP = horseradish peroxidase) or Faradaic impedance spectroscopy, respectively.



Angew. Chem. **2002**, *114*, 3548 – 3552

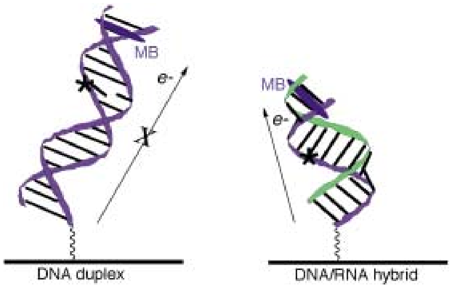
F. Patolsky, E. Katz,
I. Willner* .... 3398 – 3402

Amplified DNA Detection by Electrogenerated Biochemiluminescence and by the Catalyzed Precipitation of an Insoluble Product on Electrodes in the Presence of the Doxorubicin Intercalator

Keywords: biosensors · DNA recognition · DNA · electroluminescence · impedance spectroscopy · intercalations

---

The preferred base-stacking orientation of a conformationally constrained nucleotide (3′-*endo*-locked) within DNA/DNA and DNA/RNA duplexes (see picture) was probed by charge transport through DNA-modified gold electrode surfaces. The conformation of the sugar is seen to sensitively determine the local stacking of the duplex. These results illustrate the utility of DNA-mediated charge transport through DNA-modified surfaces in characterizing small perturbations in DNA stacking and structure.



Angew. Chem. **2002**, *114*, 3552 – 3555

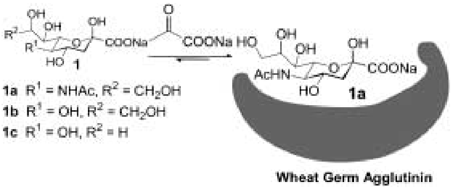
E. M. Boon, J. K. Barton,*
P. I. Pradeepkumar, J. Isaksson, C. Petit,
J. Chattopadhyaya* .... 3402 – 3405

An Electrochemical Probe of DNA Stacking in an Antisense Oligonucleotide Containing a C3′-*endo*-Locked Sugar

Keywords: antisense oligonucleotides · charge transfer · DNA · DNA-modified surfaces · nucleotides

---

Reversible formation of carbon–carbon bonds under physiological conditions by enzyme catalysis allows the generation and in situ screening of a dynamic mixture of biologically significant compounds. Generation of the dynamic library by incubation of the three sugars **1a–c** with two equivalents of sodium pyruvate in the presence of *N*-acetylneuraminic acid aldolase and wheat germ agglutinin resulted in amplification of sialic acid **1a** (see scheme).



Angew. Chem. **2002**, *114*, 3555 – 3557

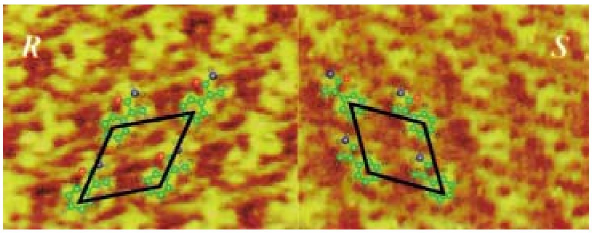
R. J. Lins, S. L. Flitsch,* N. J. Turner,*
E. Irving, S. A. Brown ...... 3405 – 3407

Enzymatic Generation and In Situ Screening of a Dynamic Combinatorial Library of Sialic Acid Analogues

Keywords: aldolase · combinatorial chemistry · dynamic libraries · enzymes · sialic acid

---

Pricking the surface of chirality: The chirality of (*R*)- and (*S*)-2-phenylpropionamide molecules has been directly observed on Cu(111) in solution by using electrochemical scanning tunneling microscopy (see images). Around the chiral center, the methyl and $CONH_2$ groups maintain the chiral configuration, although the *R* and *S* molecules adsorb onto Cu(111) in the same (4 × 4) symmetry array.



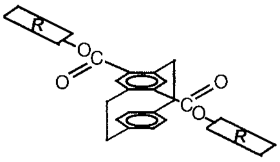
Angew. Chem. **2002**, *114*, 3558 – 3561

Q.-M. Xu, D. Wang, L.-J. Wan,* C. Wang,
C.-L. Bai,* G.-Q. Feng,
M.-X. Wang* .... 3408 – 3411

Discriminating Chiral Molecules of (*R*)-PPA and (*S*)-PPA in Aqueous Solution by ECSTM

Keywords: adsorption · chirality · copper · scanning probe microscopy · surface chemistry

The way in which chirality is introduced in a mesogenic molecule is important for determining the properties of the resultant liquid-crystalline material. The thermotropic liquid-crystalline compounds (see figure) based on planar, chiral [2.2]paracyclophane (PC) exhibit stable mesophases over a wide temperature range, while the mesophase type could be tuned by altering the nature of the substituents in the PC unit. The planar chiral PC derivatives also reveal a sufficiently high twisting ability in a nematic host.



Angew. Chem. **2002**, *114*, 3561 – 3564

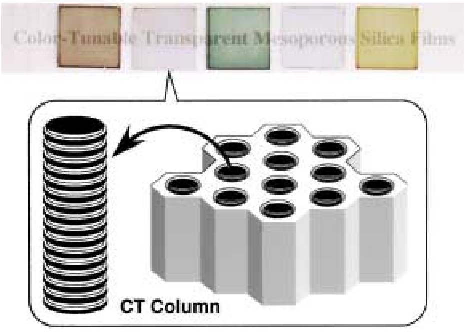
E. L. Popova, V. I. Rozenberg,
Z. A. Starikova, S. Keuker-Baumann,
H.-S. Kitzerow, H. Hopf* . . . 3411 – 3414

Thermotropic Liquid Crystals from Planar Chiral Compounds: Optically Active Mesogenic [2.2]Paracyclophane Derivatives

Keywords: chiral resolution · chirality · cyclophanes · liquid crystals

---

Physical stabilization of triphenylene-based charge-transfer complexes by hexagonally aligned silica channels enables the preparation of color-tunable, highly transparent mesoporous silica films (see picture). The donor/acceptor molar ratio was varied over a wide range (1:1 to 9:1) with the included charge-transfer complexes exhibiting unique red-shifted absorption bands.



Angew. Chem. **2002**, *114*, 3564 – 3567

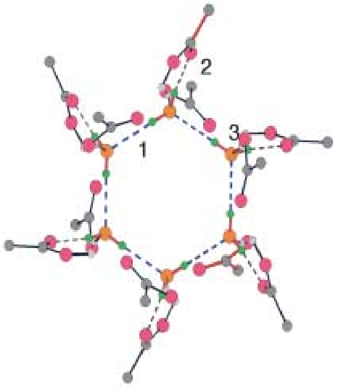
A. Okabe, T. Fukushima, K. Ariga,
T. Aida* . . . . 3414 – 3417

Color-Tunable Transparent Mesoporous Silica Films: Immobilization of One-Dimensional Columnar Charge-Transfer Assemblies in Aligned Silicate Nanochannels

Keywords: charge transfer · donor-acceptor systems · mesoporous materials · silicates · thin films

---

Trapped water: Six molecules of water are trapped in the crystal lattice of an organic supramolecular complex with bimesityl-3,3′-dicarboxylic acid in the form of a planar cyclic "ring", which is the basic structural motif of Ice II. The water molecules of the hexamer (see picture) are associated in the crystal lattice by eighteen O−H ⋯ O hydrogen bonds.



Angew. Chem. **2002**, *114*, 3567 – 3570

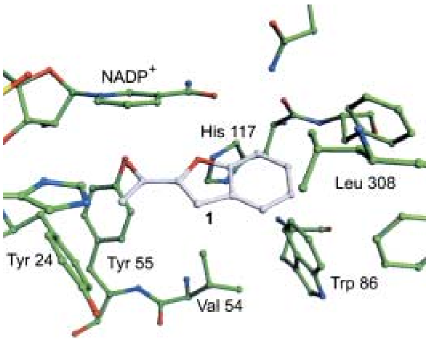
J. N. Moorthy,* R. Natarajan,
P. Venugopalan* . . . . 3417 – 3420

Characterization of a Planar Cyclic Form of Water Hexamer in an Organic Supramolecular Complex: An Unusual Self-Assembly of Bimesityl-3,3′-Dicarboxylic Acid

Keywords: carboxylic acids · cluster compounds · hydrogen bonds · supramolecular chemistry · water chemistry

---

Binding is good, displacing is better. By adding a weakly binding reporter ligand to a mixture of protein and test compounds, NMR screening can identify strongly binding ligands by observing the displacement of the reporter ligand. For example, NMR screening identified, as a reporter ligand, a small fragment, 2-acetylbenzofuran (**1,** gray skeleton), which binds to the active site of 3α-HSD. A molecular model of the complex between 3α-HSD and **1** is shown.



Angew. Chem. **2002**, *114*, 3570 – 3573

W. Jahnke,* P. Floersheim, C. Ostermeier,
X. Zhang, R. Hemmig, K. Hurth,
D. P. Uzunov . . . . 3420 – 3423

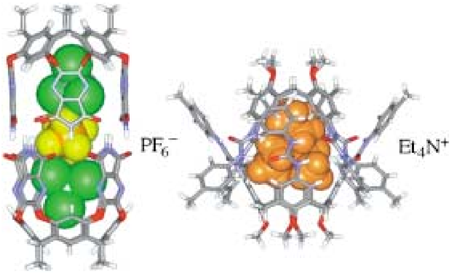
NMR Reporter Screening for the Detection of High-Affinity Ligands

Keywords: drug design · high-throughput screening · inhibitors · NMR spectroscopy · structure – activity relationships

1433-7851/02/4118-3305 $ 20.00+.50/0

Anions can be "isolated" along with one or two solvent molecules through reversible encapsulation. Cations and anions such as Et_4N^+ and PF_6^- can be further separated in solution by placement in different capsules (see picture).

Angew. Chem. **2002**, *114*, 3573–3576



O. Hayashida, A. Shivanyuk,
J. Rebek, Jr.* 3423–3426

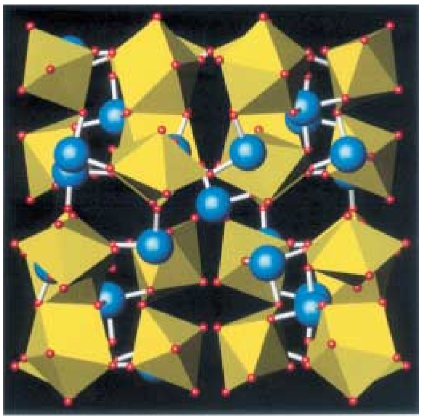
Molecular Encapsulation of Anions in a Neutral Receptor

Keywords: anions • host–guest systems • ion pairs • molecular recognition • self-assembly

---

Under hydrothermal reaction conditions, two new uranyl tellurites, $Tl_2[UO_2(TeO_3)_2]$ (**1**) and $Na_8[(UO_2)_6(TeO_3)_{10}]$ (**2**), have been prepared. These compounds display unusual bonding characteristics in that **1** contains $[Te_2O_6]^{4-}$ ions formed from two TeO_3^{2-} ions, and **2** (see picture) possesses a chiral three-dimensional network structure. The bonding and physical properties of these compounds are discussed.

Angew. Chem. **2002**, *114*, 3576–3579



P. M. Almond, M. L. McKee,
T. E. Albrecht-Schmitt* 3426–3429

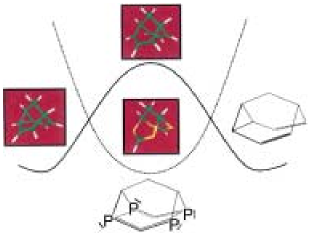
Unusual Uranyl Tellurites Containing $[Te_2O_6]^{4-}$ Ions and Three-Dimensional Networks

Keywords: actinides • hydrothermal synthesis • oxo ligands • tellurium

---

A homoaromatic C_{2v}-symmetric tetraphosphabarbaralane is the candidate for the first barbaralane derivative with "inverse" barrier to Cope rearrangement according to quantum chemical calculations (see scheme) as its C_s-symmetric form with localized double bonds is higher in energy.

Angew. Chem. **2002**, *114*, 3579–3583



M. Reiher,* B. Kirchner* . . . 3429–3433

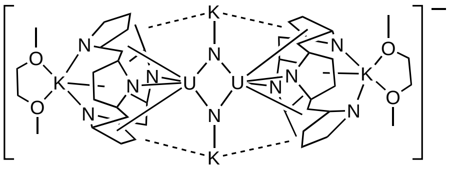
A C_{2v}-Symmetric Barbaralane

Keywords: ab initio calculations • barbaralanes • fluxionality • rearrangement • phosphorus heterocycles

---

The importance of atmosphere: The reaction of $[(Et_8\text{-calix[4]tetrapyrrole})U(dme)][K(dme)]$ and [K(naphthalenide)] yields remarkable dimeric complexes, the structures of which are dependent on the atmospheric gases employed. Reaction under N_2 leads to dinitrogen cleavage and a μ-K–N bridged dimer (see picture). In contrast, reactions performed in an Ar atmosphere promoted solvent deoxygenation, as well as reaction with silicon grease. dme = 1,2-Dimethoxyethane.

Angew. Chem. **2002**, *114*, 3583–3586



I. Korobkov, S. Gambarotta,*
G. P. A. Yap 3433–3436

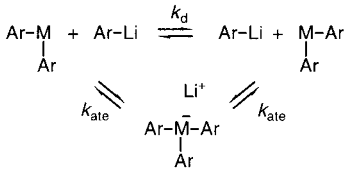
A Highly Reactive Uranium Complex Supported by the Calix[4]tetrapyrrole Tetraanion Affording Dinitrogen Cleavage, Solvent Deoxygenation, and Polysilanol Depolymerization

Keywords: cleavage reactions • dimerization • mixed-valent compounds • nitrogen fixation • uranium

---

Li/Te exchange via the ate complex with no contribution from direct exchange (i.e., $k_d = 0$) was demonstrated by NMR studies on an intermolecular reaction (see scheme; M = Te, Ar = 5-diphenylphosphanyl-2-thienyl). In contrast, in an intramolecular Li/Se exchange reaction, direct exchange bypasses the observable ate complex ($k_d \gg k_{ate}$).

Angew. Chem. **2002**, *114*, 3586–3589

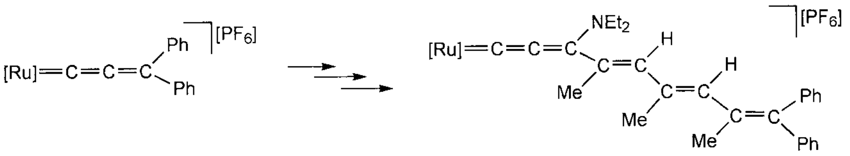


H. J. Reich,* M. J. Bevan,
B. Ö. Gudmundsson,
C. L. Puckett 3436–3439

Are Ate Complexes True Intermediates in Lithium–Metalloid Exchange? Subtle Effects of Ion-Pair Structure in Lithium–Tellurium and Lithium–Selenium Exchange Reactions

Keywords: ate complexes • lithiation • NMR spectroscopy • selenium • tellurium

Three-fold sequential insertion of the ynamine $MeC\equiv CNEt_2$ into ruthenium(II) allenylidene complexes leads to the stereoselective formation of the polyunsaturated complex **I**.



I

Angew. Chem. **2002**, *114*, 3589–3592

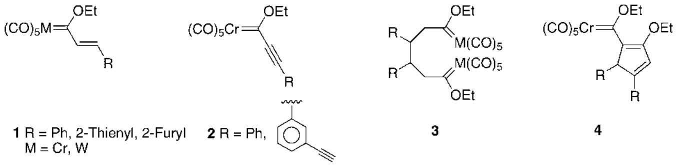
S. Conejero, J. Díez, M. P. Gamasa,
J. Gimeno,*
S. García-Granda 3439–3442

Generation of Polyunsaturated Cumulene Chains by Unprecedented Insertions of the Ynamine $MeC\equiv CNEt_2$ in Ruthenium(II) Allenylidene Complexes

Keywords: allenylidene ligands · insertion · ruthenium · cumulenes · ynamines

---

Cunning carbene chemistry: Potassium-graphite (C_8K) promotes the self condensation (to give compounds **3**) and self-condensation-cycloisomerization (to give compounds **4**) of α,β-unsaturated Fischer carbene complexes **1** and **2**, respectively. The reaction occurs through radical-anion intermediates that dimerize in a tail-to-tail fashion.



Angew. Chem. **2002**, *114*, 3592–3595

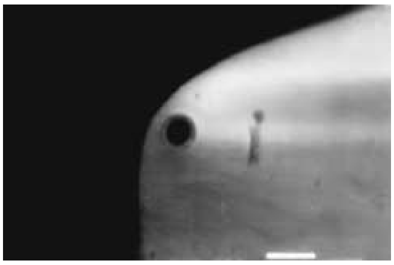
M. A. Sierra,* P. Ramírez-López,
M. Gómez-Gallego, T. Lejon,
M. J. Mancheño 3442–3445

C_8K-Promoted Self-Condensation and Self-Condensation-Cycloisomerization Reactions of α,β-Unsaturated Fischer Carbene Complexes

Keywords: carbene ligands · C–C coupling · chromium · dimerization · radical ions · tungsten

---

A nanometer-sized pipet that really works! A tiny glass pipet (shown in the figure; scale bar = 1 μm) filled with an electrolyte solution acts as the tip for scanning electrochemical microscopy. It can be used to evaluate the kinetic behavior of a recycling of charge between two molecular interfaces, such as the immiscible phases water and 1,2-dichloroethane.



Angew. Chem. **2002**, *114*, 3595–3598

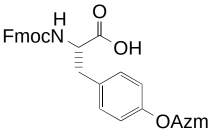
P. Sun, Z. Zhang, Z. Gao,
Y. Shao* 3445–3448

Probing Fast Facilitated Ion Transfer across an Externally Polarized Liquid–Liquid Interface by Scanning Electrochemical Microscopy

Keywords: electrochemistry · interfaces · ion transfer · nanostructures · scanning probe microscopy

---

Reversible blockage of the tyrosine phenol group leads to an efficient solid-phase strategy for the synthesis of sulfated peptides using an azidomethyl (Azm) protected tyrosine building block (**1**). The protected tyrosine derivative is compatible with standard conditions for amide-bond formation. A monosulfated and a trisulfated octapeptide fragment were assembled using this strategy.



1

Angew. Chem. **2002**, *114*, 3599–3601

T. Young, L. L. Kiessling* 3449–3451

A Strategy for the Synthesis of Sulfated Peptides

Keywords: lectins · peptides · protecting groups · solid-phase synthesis · sulfonation

Thermal decomposition of the respective trisulfides in a reducing (H_2/inert gas) atmosphere has enabled nanotubes of HfS_2, ZrS_2, and TiS_2 to be synthesized and characterized. The dimensions of the nanotubes formed depend on the Group 4 metal used. The transmission electron micrograph image shows nanotubular structures of HfS_2 with outer diameters of 55–60 nm and inner core diameters of 17–30 nm.

Angew. Chem. **2002**, *114*, 3601–3604

M. Nath, C. N. R. Rao* 3451–3454

Nanotubes of Group 4 Metal Disulfides

Keywords: electron microscopy · hafnium · nanostructures · nanotubes · X-ray diffraction

---

An exchange is better than a rest: An NMR screening method is described which facilitates the screening of compound mixtures for components that bind protein drug targets. The approach allows detection of active molecules thanks to a "probe" molecule, which competes with a library of potential ligands for binding sites on a targeted protein. The whole spectrum of active ligands, including those displaying either very fast or very slow exchange behavior, are equally susceptible to detection by this method.

Angew. Chem. **2002**, *114*, 3604–3607

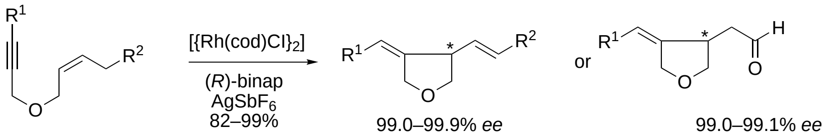
A. H. Siriwardena,* F. Tian, S. Noble,
J. H. Prestegard 3454–3457

A Straightforward NMR-Spectroscopy-Based Method for Rapid Library Screening

Keywords: carbohydrates · competitive binding · drug design · high-throughput screening · NMR spectroscopy

---

Over 99 % *ee* was obtained for all the tested substrates in a Rh-catalyzed Alder–ene reaction. Simply mixing air-stable, commercially available [{Rh(cod)Cl}$_2$] (cod = 1,5-cyclooctadiene) and 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (binap) at room temperature afforded functionalized and chiral tetrahydrofurans in high yields with high efficiency (turnover frequency: 1500 h^{-1}). The catalyst loading was as low as 0.8 mol %.



R^1 = aryl, alkyl, carbonyl, alkoxy, hydroxy
R^2 = H, alkyl, acetoxy, alkoxy

Angew. Chem. **2002**, *114*, 3607–3610

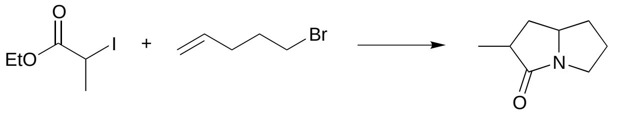
A. Lei, M. He, S. Wu,
X. Zhang* 3457–3460

Highly Enantioselective Rh-Catalyzed Intramolecular Alder–Ene Reactions for the Syntheses of Chiral Tetrahydrofurans

Keywords: enantioselectivity · heterocycles · homogeneous catalysis · rhodium · synthetic methods

---

A one-pot intermolecular radical carboazidation of alkenes is reported. The utility of the reaction is demonstrated by the development of a three-component preparation of pyrrolidinones, pyrrolizidinones [Eq. (a)], and indolizidinones starting from benzenesulfonyl azide, terminal alkenes, and 2-iodoesters.



(a)

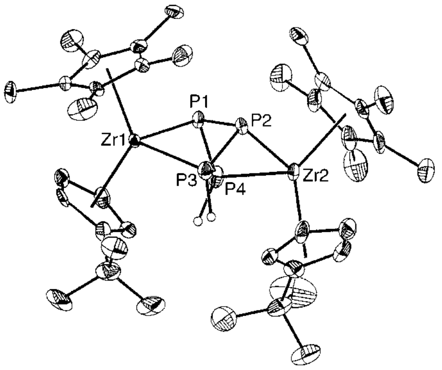
Angew. Chem. **2002**, *114*, 3611–3612

P. Renaud,* C. Ollivier,
P. Panchaud 3460–3462

Radical Carboazidation of Alkenes: An Efficient Tool for the Preparation of Pyrrolidinone Derivatives

Keywords: alkaloids · aminations · azides · C–C coupling · radical reactions

Hydrogenation of white phosphorus (P_4) has been achieved under ambient conditions by reaction with $[Zr(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4t\text{Bu})H_2]$ to give $[\{Zr(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4t\text{Bu})\}_2(P_4)H_2]$ (see picture). Preliminary data suggest that the reaction proceeds by a cooperative reductive elimination/insertion sequence involving two zirconium centers.



Angew. Chem. **2002**, *114*, 3613 – 3615

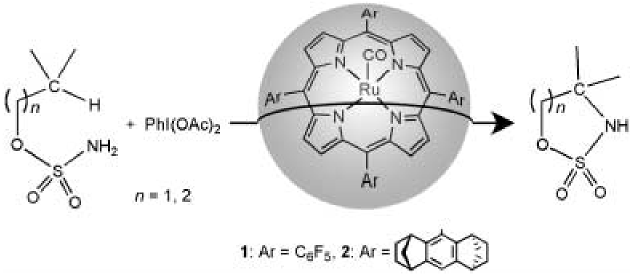
P. J. Chirik,* J. A. Pool,
E. Lobkovsky .... 3463 – 3465

Functionalization of Elemental Phosphorus with $[Zr(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4t\text{Bu})H_2]_2$

Keywords: elimination • hydrogenation • insertion • phosphorus • zirconium

---

Virtually complete diastereoselectivity is observed in the intramolecular amidation of saturated C–H bonds, catalyzed by the ruthenium porphyrin catalyst **1** or **2**. Reactions of sulfamate esters with $PhI(OAc)_2$ in the presence of **1** or **2** afforded cyclic sulfamidates in up to 87% *ee*.



Angew. Chem. **2002**, *114*, 3615 – 3618

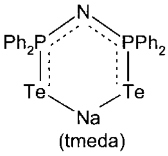
J.-L. Liang, S.-X. Yuan, J.-S. Huang,
W.-Y. Yu, C.-M. Che* ...... 3465 – 3468

Highly Diastereo- and Enantioselective Intramolecular Amidation of Saturated C–H Bonds Catalyzed by Ruthenium Porphyrins

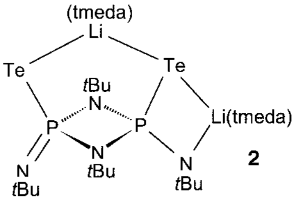
Keywords: asymmetric catalysis • cyclization • porphyrinoids • ruthenium • sulfamidates

---

Oxidation with elemental tellurium of $Na[Ph_2PNPPh_2]$ and $[Li(thf)]_2[t\text{BuNP}(\mu\text{-N}t\text{Bu})_2\text{PN}t\text{Bu}]$ in the presence of tetramethylethylenediamine (tmeda) provides access to anionic imido (**1**) and amido tellurophosphoranes (**2**). Complex **2** displays a novel tetradentate *N*,*Te*,*Te*,*Te′* bonding mode.



1



2

Angew. Chem. **2002**, *114*, 3618 – 3620

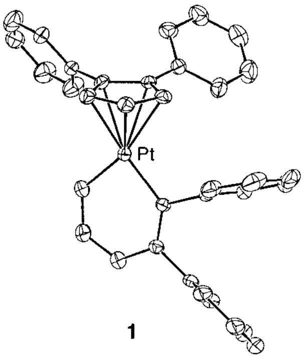
G. G. Briand, T. Chivers,*
M. Parvez .... 3468 – 3470

A New Approach to Metalated Imido and Amido Tellurophosphoranes

Keywords: alkali metals • N ligands • N,P ligands • tellurium

---

No longer limited to the classical examples of osmium- and iridium-based metallaaromatics, treatment of $[Pt(cod)Cl_2]$ with a nucleophilic 3-vinylcyclopropene yields platinabenzene **1**, which has been fully characterized by NMR spectroscopy and X-ray crystallography.



Angew. Chem. **2002**, *114*, 3620 – 3623

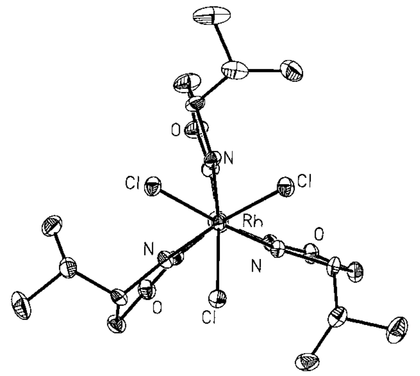
V. Jacob, T. J. R. Weakley,
M. M. Haley* .... 3470 – 3473

Metallabenzenes and Valence Isomers: Synthesis and Characterization of a Platinabenzene

Keywords: aromaticity • metallacycles • platinum • structure elucidation

1433-7851/02/4118-3309 $ 20.00+.50/0

A new class of tripodal ligands, chiral 1,1,1-tris(oxazolinyl)ethane derivatives, has been synthesized by using a *modular* approach by coupling of mono- with bisoxazoline derivatives. This method allows the facile access to symmetrically (C_3-chiral, as shown for the rhodium complex) or unsymmetrically substituted (C_1-chiral) ligands. Their copper(I) complexes have been used as catalysts in the asymmetric cyclopropanation of styrene.



Angew. Chem. **2002**, *114*, 3623–3625

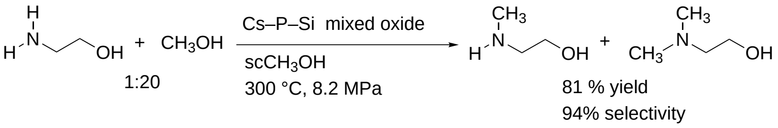
S. Bellemin-Laponnaz,
L. H. Gade* 3473–3475

A Modular Approach to C_1 and C_3 Chiral N-Tripodal Ligands for Asymmetric Catalysis

Keywords: asymmetric catalysis · chirality · N,O ligands · tripodal ligands

---

The unique properties of supercritical fluids can be exploited for fine-tuning product selectivity. Under the conditions listed for the N-methylation of amino alcohols (see scheme) over solid acid—base bifunctional catalysts, the total yield and product selectivity could be improved. Enhanced product selectivity might be attributed to the milder reaction conditions possible with supercritical methanol, as well as the increased concentration of methanol on the catalyst.



Angew. Chem. **2002**, *114*, 3626–3629

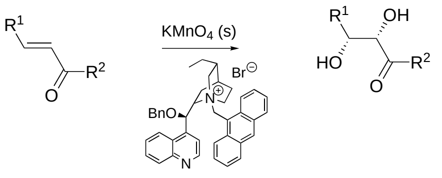
T. Oku, T. Ikariya* 3476–3479

Enhanced Product Selectivity in Continuous N-Methylation of Amino Alcohols over Solid Acid–Base Catalysts with Supercritical Methanol

Keywords: alkylation · amino alcohols · heterogeneous catalysis · supercritical fluids

---

Enantiomerically enriched 1,2-diols can be prepared, in good enantiomeric excesses, by using a novel asymmetric dihydroxylation of enones with permanganate under phase-transfer conditions (see scheme: e.g. $R^1 = n$Bu, $R^2 = (p\text{-OMe})C_6H_4$).



Angew. Chem. **2002**, *114*, 3629–3630

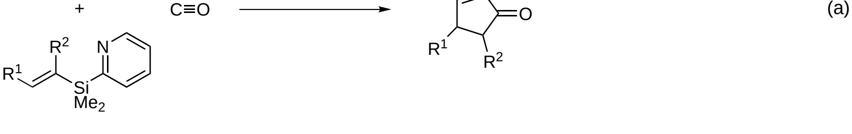
R. A. Bhunnoo, Y. Hu, D. I. Lainé,
R. C. D. Brown* 3479–3480

An Asymmetric Phase-Transfer Dihydroxylation Reaction

Keywords: asymmetric synthesis · dihydroxylation · diols · oxidation · phase-transfer catalysis

---

Now even unstrained alkenes can be used in catalytic intermolecular Pauson–Khand reactions [Eq. (a)]. This is made possible by the use of the directing group dimethyl(2-pyridyl)silyl, which can be easily removed at the end of the reaction. Furthermore, one observes completely regioselective incorporation of substituents at the 4- and 5-positions of the 2-cyclopentenone structure.



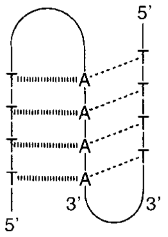
Angew. Chem. **2002**, *114*, 3631–3634

K. Itami,* K. Mitsudo,
J.-i. Yoshida* 3481–3484

A Pyridylsilyl Group Expands the Scope of Catalytic Intermolecular Pauson–Khand Reactions

Keywords: alkenes · alkynes · cycloadditions · homogeneous catalysis · silanes

Exciting DNA threesome: Time-resolved transient absorption spectroscopy has been used to study electron-transfer processes between an excited-state electron acceptor and a ground-state electron donor, separated by a variable number of T:A·T triplet steps in triplex DNA (see figure). The formation and decay of both the acceptor anion radical and donor cation radical can be resolved. Electron tunneling is more effective at longer acceptor–donor distances in triplex than in duplex DNA.



F. D. Lewis,* Y. Wu, R. T. Hayes,
M. R. Wasielewski* 3485–3487

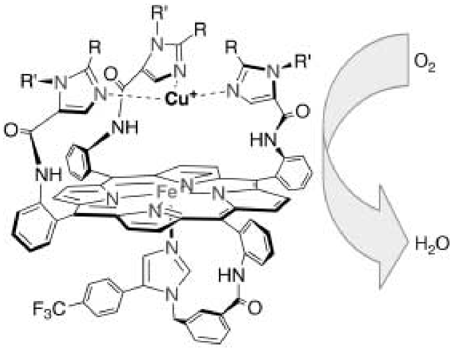
DNA-Mediated Electron Transfer across Synthetic T:A·T Triplex Structures

Angew. Chem. **2002**, *114*, 3635–3637

Keywords: DNA structures · electron transfer · fluorescence spectroscopy · hole transport · time-resolved spectroscopy

---

Close structural analogues (see picture) of the O_2-reducing site of terminal oxidases dispersed in a phospholipid reduce O_2 at physiological potentials and do not release toxic partially reduced oxygen by-products, even when electron flux is diffusion-limited.



J. P. Collman,* R. Boulatov 3487–3489

Electrocatalytic O_2 Reduction by Synthetic Analogues of the Heme/Cu Site of Cytochrome Oxidase Incorporated in a Lipid Film

Angew. Chem. **2002**, *114*, 3637–3639

Keywords: bioinorganic chemistry · electrochemistry · oxidoreductases · phospholipids · porphyrinoids

---

Casting silica nets: By repeated "nanocasting" it is possible to first obtain a negative of the SBA-15 structure, known as CMK-3, which is then used to produce another nanocast by impregnation with tetraethoxysilane and condensation. After calcination to remove the carbon, an ordered mesoporous silica is obtained, called NCS-1 (see scheme). This pathway could be generalized to allow also the synthesis of other ordered oxides.

A.-H. Lu, W. Schmidt, A. Taguchi,
B. Spliethoff, B. Tesche,
F. Schüth* 3489–3492

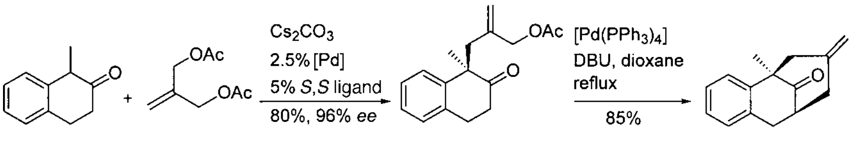
Taking Nanocasting One Step Further: Replicating CMK-3 as a Silica Material

Angew. Chem. **2002**, *114*, 3639–3642

Keywords: mesoporous materials · nanocasting · silicon · zeolite analogues

---

Quaternary centers can be created asymmetrically in high enantiomeric excess by the proper choice of ligand and metal cation in the Pd-catalyzed asymmetric allylic alkylation of α-aryl ketones. A broad range of ketone enolates can be tolerated in the reaction, as illustrated by the synthesis of conformationally constrained β-tetralone in 96% *ee* (see scheme, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene).



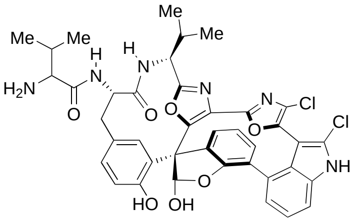
B. M. Trost,* G. M. Schroeder,
J. Kristensen 3492–3495

Palladium-Catalyzed Asymmetric Allylic Alkylation of α-Aryl Ketones

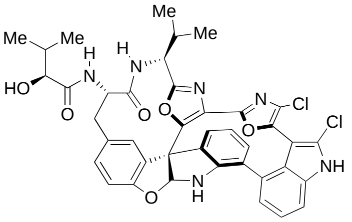
Angew. Chem. **2002**, *114*, 3642–3645

Keywords: aryl ketones · asymmetric catalysis · enantioselectivity · ligand effects · palladium

Ever since its discovery in 1991, diazonamide A (**1**) has been eyed by synthetic chemists as a potential target because of its puzzling molecular architecture and potent biological activity. The race to synthesize this intriguing natural product was further complicated at the end of last year when a synthesis was completed only to prove that the originally proposed structure was in error. The new structural assignment (**2**) required retooling of synthetic strategies toward the new target. A total synthesis of diazonamide A has now been achieved confirming its newly proposed structure.



1: original structure of diazonamide A



2: revised structure of diazonamide A

Angew. Chem. **2002**, *114*, 3645–3649

Keywords: antitumor agents · cyclization · macrocycles · natural products · total synthesis

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

Accelerated publications

* Author to whom correspondence should be addressed

BOOKS

WEB SITES

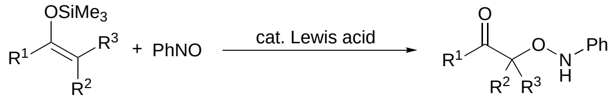
SERVICE

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

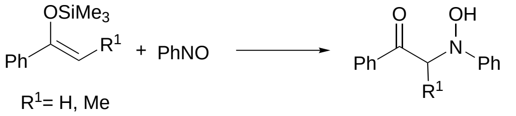
CORRIGENDA

In the Communication by **J. Rademann** and **M. Barth** in issue 16, **2002**, pp. 2975–2978, the single-letter codes for the amino acids of peptide **15** (H-Trp-Glu-Ile-His-Asn-Ala-Cys-His-Thr-Ser-Thr-Ala-Gly-OH), WEIHNACHTSTAG, was erroneously printed as "Christmas". The editorial office apologizes for this error.

In the Communication by **N. Momiyama** and **H. Yamamoto**, in issue 16, **2002**, pp. 2986–2988, Equations 1 and 2 (shown below) were omitted in the final print version. The correct version of this paper can be found on the Wiley InterScience Website at www.interscience.wiley.com. The editorial office apologizes for this error.



(1)



(2)