



The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

C. Hawner, K. Li, V. Cirriez, A. Alexakis*

Copper-Catalyzed Asymmetric Conjugate Addition of Aryl Aluminum Reagents to Trisubstituted Enones: Construction of Aryl-Substituted Quaternary Centers

K. W. Eberhardt, C. L. Degen, A. Hunkeler, B. H. Meier*

One- and Two-Dimensional NMR Spectroscopy with a Magnetic-Resonance Force Microscope

S. Wan, J. Guo, J. Kim, H. Ihee, D. Jiang*

A Belt-Shaped, Blue-Luminescent and Semiconducting Covalent Organic Framework

R. E. Jilek, M. Jang, E. D. Smolensky, J. D. Britton, J. E. Ellis*

Structurally Distinct Homoleptic Anthracene Complexes $[M(C_{14}H_{10})_3]^{2-}$, $M=Ti, Zr, Hf$: Tris(arene) Complexes for a Triad of Transition Metals

M. Inoue,* N. Lee, K. Miyazaki, T. Usuki, S. Matsuoka, M. Hirama*

Critical Importance of the Nine-Membered F Ring of Ciguatoxin for Potent Bioactivity: Total Synthesis and Biological Evaluation of F-Ring-Modified Analogues

J. Steill, J. Zhao, C.-K. Siu, Y. Ke, U. H. Verkerk, J. Oomens,

R. C. Dunbar, A. C. Hopkinson, K. M. Siu*

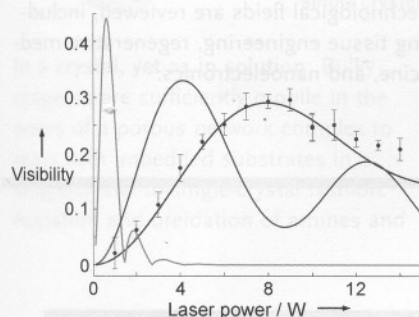
Structure of the Observable Histidine Radical Cation in the Gas Phase: a Captodative α Radical Ion

Tomorrow's Chemistry Today

Bruno Pignataro

Books

reviewed by G. B. Kauffman 7988



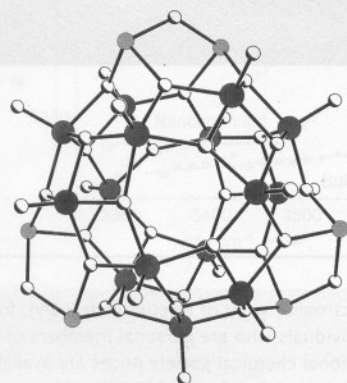
The perfect wave: The wave properties of large molecules have been used for mass spectrometry. A perfluoroalkylated palladium complex has been investigated by this method and its mass and polarizability determined from the visibility of the molecules interferogram. This method allows the differentiation of molecule fragments in the source from those generated in the detector. Applications based on matter waves are now conceivable.

Highlights

Mass Spectrometry

K.-O. Greulich* 7990–7991

The Wave Property of Heavy Molecules—Its Use in Mass Spectrometry



Quantum leap: Recent observations using pulsed EPR spectroscopy suggest that it is possible magnetic molecules such as the $\{V_{15}\}$ polyoxometalate cage (see picture; V red, As blue, O white) could be used in quantum information processing (QIP). Controlled interactions of cage complexes with an $S=1/2$ ground state, acting as qubits, could allow QIP.

Quantum Computing

R. E. P. Winpenny* 7992–7994

Quantum Information Processing Using Molecular Nanomagnets As Qubits

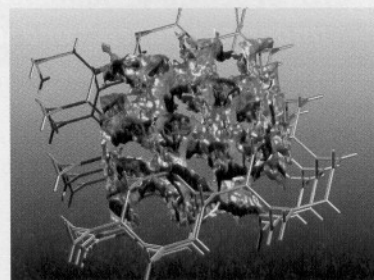
Essays

Chemical Geometry

S. T. Hyde,* M. O'Keeffe,
D. M. Proserpio — 7996–8000

A Short History of an Elusive Yet
Ubiquitous Structure in Chemistry,
Materials, and Mathematics

Beauty in the sciences: The extraordinary history of a three-periodic net and its associated surface, the gyroid, is recounted (see picture). These structures appear in diverse contexts in mathematics, as the topology for crystal structures in materials, which is the basis for liquid crystal phases and derived mesoporous materials, and in insect pigments.

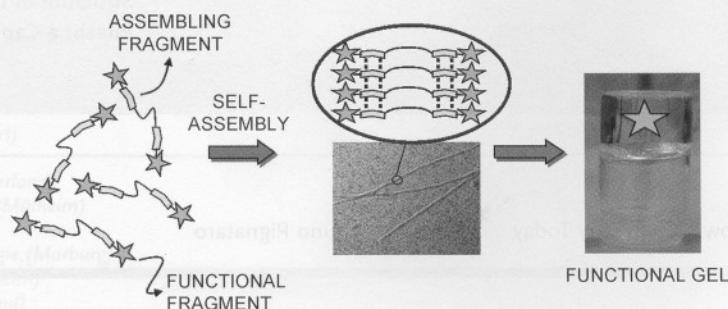


Reviews

Gel Materials

A. R. Hirst,* B. Escuder, J. F. Miravet,
D. K. Smith* — 8002–8018

High-Tech Applications of Self-
Assembling Supramolecular
Nanostructured Gel-Phase Materials:
From Regenerative Medicine to Electronic
Devices



Starting to gel: Recent developments in self-assembling low-molecular-weight gelators has led to rationally designed materials with increasingly advanced and specialized applications. Recent demon-

strations of molecular gels in diverse technological fields are reviewed, including tissue engineering, regenerative medicine, and nanoelectronics.

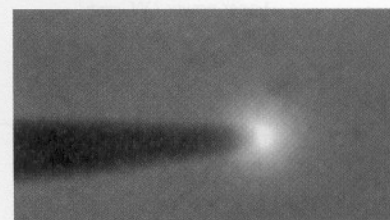
Communications

VIP Plasma Chemistry

D. Staack, A. Fridman, A. Gutsol,
Y. Gogotsi,* G. Friedman* — 8020–8024

Nanoscale Corona Discharge in Liquids,
Enabling Nanosecond Optical Emission
Spectroscopy

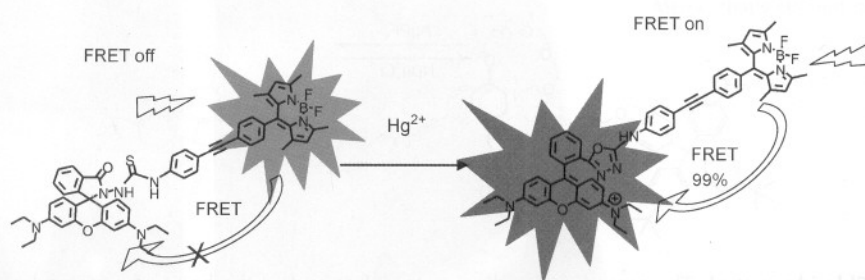
My corona! A nonthermal corona discharge inside a liquid medium around electrodes with ultrasharp tips or elongated nanoparticles allows simultaneous chemical analysis of multiple dissolved elements within nanoseconds. The proposed optical emission spectroscopy method can be applied for ultrafast time-resolved multielemental analysis of femtoliter volumes of liquid with a one-micrometer spatial resolution.



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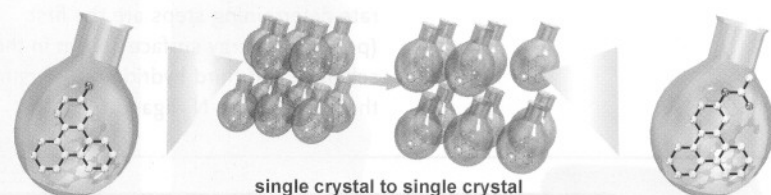
Mercury rising: A FRET-based ratiometric probe (see picture; FRET = fluorescence resonance energy transfer) can selectively detect Hg^{2+} ions on the parts-per-billion scale under physiological conditions. The probe undergoes a clear Hg^{2+} -induced

change in the intensity ratio of the two well-separated and equally intense emission bands of dipyrrometheneboron difluoride and rhodamine. Experiments show that the probe can be used in living cells.

Fluorescent Probes

X. Zhang, Y. Xiao,* X. Qian* 8025–8029

A Ratiometric Fluorescent Probe Based on FRET for Imaging Hg^{2+} Ions in Living Cells



single crystal to single crystal

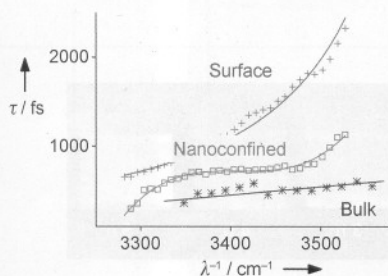
In a crystal, yet as in solution: Bulky reagents are sufficiently mobile in the pores of a porous network complex to react with imbedded substrates in a single-crystal-to-single-crystal fashion. Acylation and ureidation of amines and

Schiff-base formation from aldehydes occur efficiently. The pore of the complex thus serves as a crystalline molecular flask, where reaction products are simply determined by X-ray crystallographic analysis.

Molecular Flasks

T. Kawamichi, T. Kodama, M. Kawano,* M. Fujita* 8030–8032

Single-Crystalline Molecular Flasks: Chemical Transformation with Bulky Reagents in the Pores of Porous Coordination Networks



Femtosecond IR spectroscopy was used to study water confined in 1–50 nm pores. The results show that even large pores induce significant changes (for example excited-state lifetimes, see diagram) to the hydrogen-bond network, which are independent of pore diameter between 1 and 50 nm. Thus, the changes are not surface-induced but rather finite size effects, and suggest a confinement-induced enhancement of the acidic character of water.

Hydrogen Bonds

R. Musat, J. P. Renault,* M. Candelaesi, D. J. Palmer, S. Le Caër, R. Righini, S. Pommeret 8033–8035

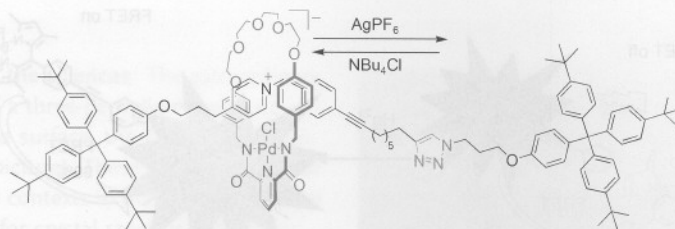
Finite Size Effects on Hydrogen Bonds in Confined Water

Rotaxanes

M. J. Barrell, D. A. Leigh,* P. J. Lusby,*
A. M. Z. Slawin — 8036–8039



An Ion-Pair Template for Rotaxane Formation and its Exploitation in an Orthogonal Interaction Anion-Switchable Molecular Shuttle



Chloride control: The serendipitous discovery of a molecular recognition motif that is triggered by the formation of an anion-palladium coordination bond is exploited as an efficient rotaxane-forming

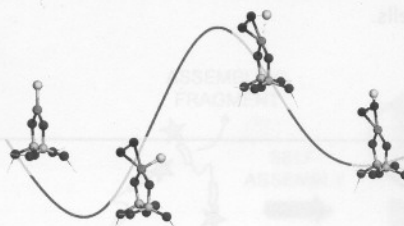
template and as the basis of a molecular shuttle. The macrocycle of this rotaxane moves between the two stations when the counterion is changed from chloride to hexafluorophosphate (see picture).

Dinitrogen Cleavage

J. Li, S. Li* — 8040–8043



Energetics and Mechanism of Dinitrogen Cleavage at a Mononuclear Surface Tantalum Center: A New Way of Dinitrogen Reduction

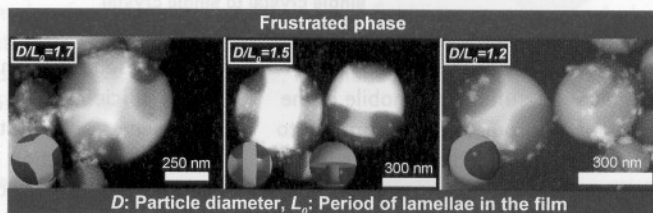
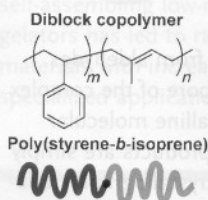


A rare side-on mode of N₂ coordination to the Ta^{III} center of [(≡SiO)₂TaH], which was found to be the active species for N₂ reduction at a mononuclear surface Ta center, is critical for the subsequent hydride-transfer steps in the cleavage of N₂ according to B3LYP calculations. The rate-determining steps are the first (potential energy surface shown in the scheme) and third hydride transfers from the metal to the N₂ ligand.

Frustrated Phases

T. Higuchi,* A. Tajima, K. Motoyoshi,
H. Yabu, M. Shimomura — 8044–8046

Frustrated Phases of Block Copolymers in Nanoparticles



D: Particle diameter, *L₀*: Period of lamellae in the film

3D confinement effect: Block copolymers form novel phase separation structures in the nanoparticles owing to frustration of the nanosized confinement effect. Whereas films of the block copolymers form lamellar structures, the nanoparti-

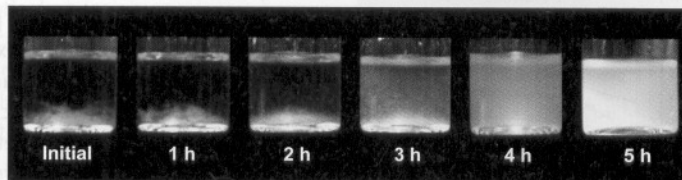
cles formed unique structures (Janus-type, tennis-ball-, mushroom-, wheel-, and screwlike structures) depending on the ratio between particle diameter and molecular weight.

Cellulose Conversion

R. Rinaldi, R. Palkovits,
F. Schüth* — 8047–8050



Depolymerization of Cellulose Using Solid Catalysts in Ionic Liquids



Wood you believe it! Solid acids act as powerful catalysts for the hydrolysis of cellulose dissolved in an ionic liquid. Cellulose undergoes selective depolymerization, yielding cellulose oligomers

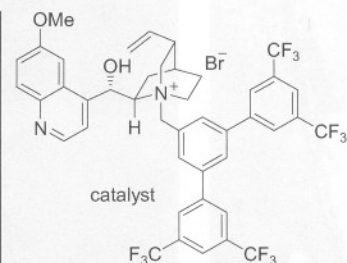
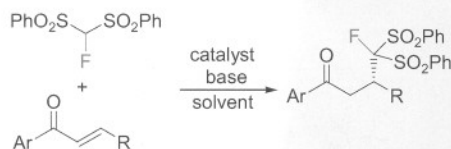
(cellooligomers) without any substantial formation of side products. Even wood, a lignocellulosic material, is hydrolyzed using this methodology.

Synthetic Methods

T. Furukawa, N. Shibata,* S. Mizuta,
S. Nakamura, T. Toru,
M. Shiro **8051–8054**



Catalytic Enantioselective Michael
Addition of 1-Fluorobis(phenylsulfonyl)-
methane to α,β -Unsaturated Ketones
Catalyzed by Cinchona Alkaloids



A catalyst worth its salt: The ammonium salts of cinchona alkaloids possessing sterically demanding substituents effectively catalyzed the enantioselective 1,4-conjugate addition of 1-fluorobis(phenylsulfonyl)methane to α,β -unsaturated

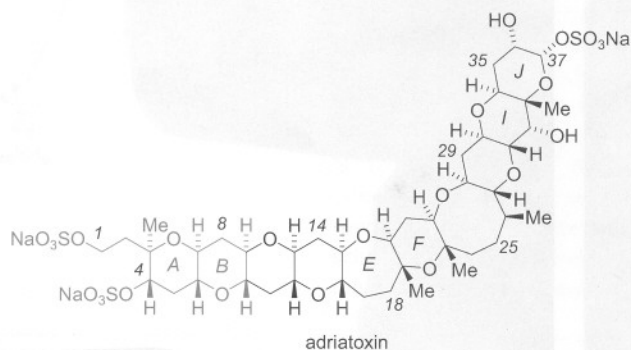
ketones to furnish the Michael adducts in high yield with excellent enantioselectivity (see scheme). The adducts are useful for the synthesis of chiral monofluoro-methylated molecules.

Natural Product Synthesis

C. Osei Akoto, J. D. Rainier* **8055–8058**



Harnessing Glycal-Epoxyde Rearrange-
ments: The Generation of the AB, EF,
and IJ Rings of Adriatoxin



Climbing the ladder: The generation of three bicyclic subunits of adriatoxin (see structure) was accomplished by using

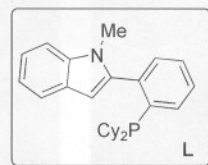
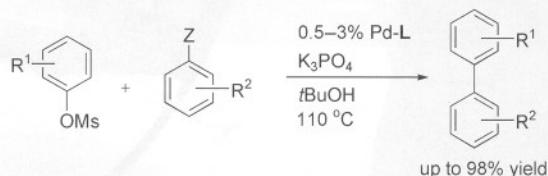
glycal-epoxide rearrangements, glycal-Claisen rearrangements, and C-glycoside-forming reactions.

Homogeneous Catalysis

C. M. So, C. P. Lau,
F. Y. Kwong* **8059–8063**



A General Palladium-Catalyzed Suzuki–
Miyaura Coupling of Aryl Mesylates



Catalyze this! The first palladium-catalyzed Suzuki–Miyaura coupling of unactivated aryl mesylates is reported, with not only arylboronic acids, but also other organoboron nucleophiles (see picture;

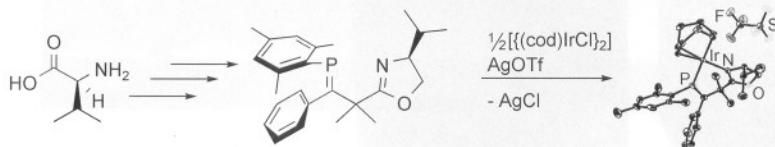
$Z = B(OH)_2, BF_3K, BPin$). The reaction conditions are compatible with various common functional groups ($R^1 = \text{alkyl, OMe, CHO, CO, CN, CO}_2R', \text{heteroaryl}$).

Low Coordinate Phosphorus

J. Dugal-Tessier, G. R. Dake,*
D. P. Gates* **8064–8067**

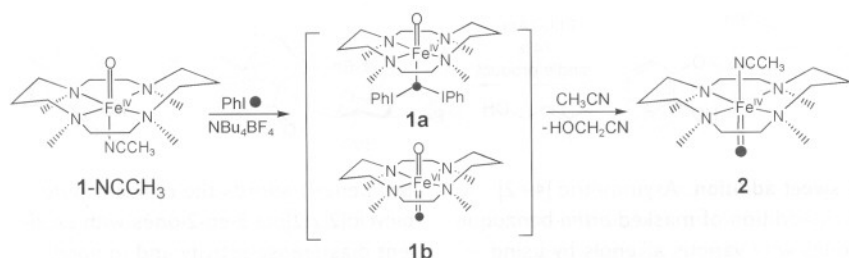


Chiral Ligand Design: A Bidentate Ligand
Incorporating an Acyclic Phosphaalkene



Simply made and stable: An asymmetric phosphoalkene has been synthesized from L-valine, a readily available chiral precursor. This air-stable ligand forms a $P(sp^2), N(sp^2)$ complex with iridium(I) (see

scheme) and is the first example of a new class of chiral phosphorus-based ligands which are expected to possess excellent π -acceptor properties.



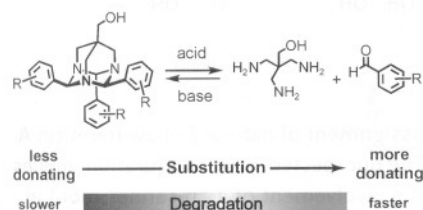
Oxoferryl gymnastics: The oxo and CH_3CN ligands in **1-NCCH₃** can swap positions in the presence of iodosobenzene and tetrafluoroborate anion leading

to the generation of a more reactive isomer **2**. This conversion is proposed to take place via an activated Fe^{IV} unit (**1a**) or a transient dioxoiron(VI) species (**1b**).

Iron Oxo Complexes

K. Ray, J. England, A. T. Fiedler,
M. Martinho, E. Münck,*
L. Que, Jr.* 8068–8071

An Inverted and More Oxidizing Isomer of $[\text{Fe}^{\text{IV}}(\text{O})(\text{tmc})(\text{NCCH}_3)]^{2+}$



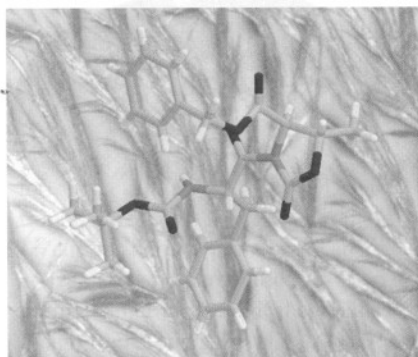
Basic groups from acid hydrolysis: 1,3,5-Triazaadamantanes (TAAs) are shown to degrade in acidic conditions to produce basic byproducts (see scheme). The rate of hydrolysis can be tuned by changing the substituents present on the aromatic rings. TAA-containing dendrimers can be synthesized readily as a result of the branched architecture of the TAA building blocks.

Tuneable Degradation

A. M. Balija, R. E. Kohman,
S. C. Zimmerman* 8072–8074

Substituted 1,3,5-Triazaadamantanes:
Biocompatible and Degradable Building
Blocks

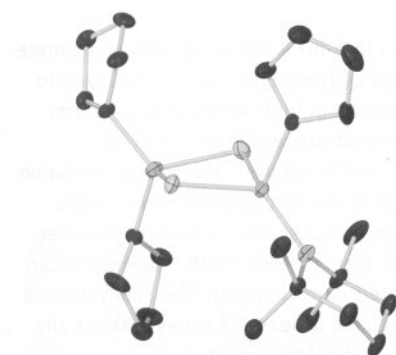
One is enough: The dipeptide Boc-L-Phe-D-Oxd-OBn (Boc = *tert*-butoxycarbonyl, Phe = phenylalanine, Oxd = 4-methyl-5-carboxy oxazolidin-2-one, Bn = benzyl; see picture; gray C, white H, red O, blue N) spontaneously forms uniform fibers consisting of parallel infinite linear chains arising from single intermolecular $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bonds. This is the absolute borderline case of a parallel β -sheet structure.



Amyloids

G. Angelici, G. Falini, H.-J. Hofmann,
D. Huster, M. Monari,
C. Tomasini* 8075–8078

A Fiberlike Peptide Material Stabilized by
Single Intermolecular Hydrogen Bonds



The molecular engines that drive enhanced magnesiations are unveiled through structural elucidation of a 2,2,6,6-tetramethylpiperidide (TMP) Hauser base and its turbo model (see structure; Mg green, Li violet, C purple, O red, N blue, Cl yellow).

Hauser Bases

P. García-Álvarez, D. V. Graham, E. Hevia,
A. R. Kennedy, J. Klett, R. E. Mulvey,*
C. T. O'Hara,
S. Weatherstone 8079–8081

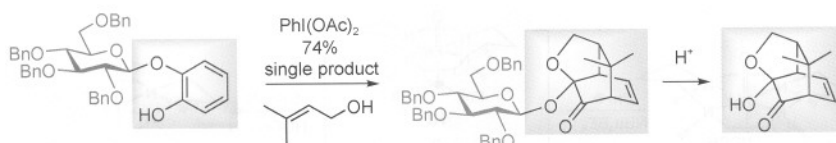
Unmasking Representative Structures of
TMP-Active Hauser and Turbo-Hauser
Bases

Asymmetric Synthesis

S.-Y. Luo, Y.-J. Jang, J.-Y. Liu, C.-S. Chu,
C.-C. Liao,* S.-C. Hung* — 8082–8085



Carbohydrate-Templated Asymmetric Diels–Alder Reactions of Masked *ortho*-Benzoquinones for the Synthesis of Chiral Bicyclo[2.2.2]oct-5-en-2-ones



A sweet addition: Asymmetric [4+2] cycloaddition of masked *ortho*-benzoquinones with various alkenols by using sugars as chiral auxiliaries (see scheme;

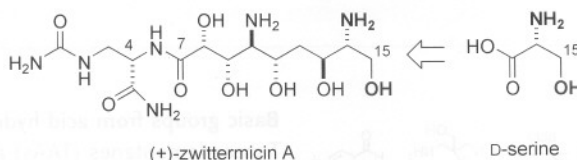
Bn: benzyl) affords the optically pure bicyclo[2.2.2]oct-5-en-2-ones with excellent diastereoselectivity and in good yields.

Natural Product Synthesis

E. W. Rogers, D. S. Dalisay,
T. F. Molinski* — 8086–8089



(+)-Zwittermicin A: Assignment of its Complete Configuration by Total Synthesis of the Enantiomer and Implication of D-Serine in its Biosynthesis



D-Serine is the prime suspect: The total synthesis of (–)-zwittermicin A has been achieved from a suitably protected C₂-symmetric diamino tetraol unit and has allowed the complete stereochemical

assignment of natural (+)-zwittermicin A. The unexpected 14*R* configuration implies the involvement of a “D-serine” motif in the biosynthesis of (+)-zwittermicin A (see scheme).

Marine Metabolites

S. H. Wright, A. Raab, J. N. Tabudravu,
J. Feldmann,* P. F. Long, C. N. Battershill,
W. C. Dunlap, B. F. Milne,
M. Jaspars* — 8090–8092



Marine Metabolites and Metal Ion Chelation: Intact Recovery and Identification of an Iron(II) Complex in the Extract of the Ascidian *Eudistoma gilboviride*



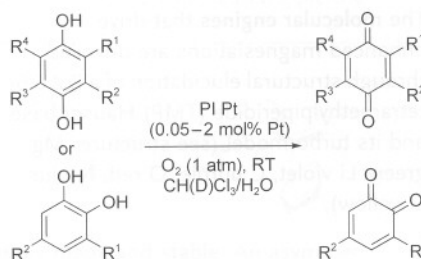
Sequestering sea squirts: Liquid chromatography with parallel inductively coupled plasma mass spectrometry/electrospray mass spectrometry was used to discover and identify novel lipophilic metal complexes in the solvent extract of the ascidian *Eudistoma gilboviride*. Using these tools it is now possible to examine whether such complexes play an integral part in an organism's physiology.

Nanoclusters

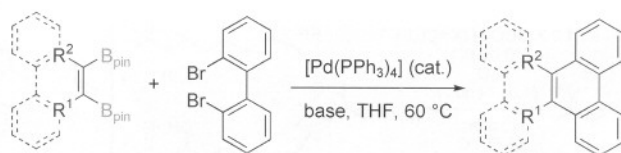
H. Miyamura, M. Shiramizu,
R. Matsubara,
S. Kobayashi* — 8093–8095



Aerobic Oxidation of Hydroquinone Derivatives Catalyzed by Polymer-Incarcerated Platinum Catalyst



It's a lock-in! A remarkably wide substrate scope of hydroquinones are oxidized to quinones in high yields in a platinum-catalyzed process with as low as 0.05 mol% catalyst. The aerobic oxidation is catalyzed by platinum nanoclusters trapped in a styrene-based polymer network (see scheme, PI Pt = polymer-incarcerated nanoclusters). The catalyst could be reused at least 13 times without any loss of catalytic activity.



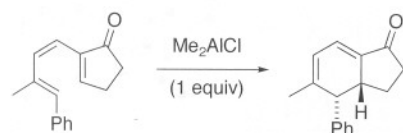
Double-cross: An annulation approach to functionalized polycyclic aromatic hydrocarbons involving a palladium-catalyzed double cross-coupling reaction of *vic*-diborylalkenes and -phenanthrenes with 2,2'-dibromobiaryls led to a variety of

phenanthrenes and dibenzo-[*g,p*]chrysenes, as well as [5]helicenes, dithienobenzenes, and triphenyleno[1,2-*b*:4,3-*b'*]dithiophenes (see scheme; B_{pin} = pinacoloboryl).

Cross-Coupling

M. Shimizu,* I. Nagao, Y. Tomioka, T. Hiyama 8096–8099

Palladium-Catalyzed Annulation of *vic*-Bis(pinacoloboryl)alkenes and -phenanthrenes with 2,2'-Dibromobiaryls: Facile Synthesis of Functionalized Phenanthrenes and Dibenzo[*g,p*]chrysenes



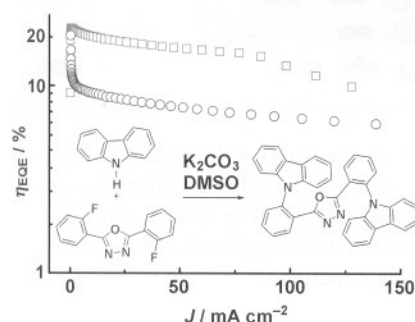
55-fold rate acceleration

Filling the gap: Lewis acid catalysis of a 6π electrocyclization has been achieved for the first time (see scheme). DFT calculations were performed on the coordination of a Lewis acid to a Lewis basic group in the 2-position of a triene, and experimentally, the rates of the electrocyclization increase in the presence of Me₂AlCl.

Electrocyclization Reaction

L. M. Bishop, J. E. Barbarow, R. G. Bergman,* D. Trauner* 8100–8103

Catalysis of 6π Electrocyclizations

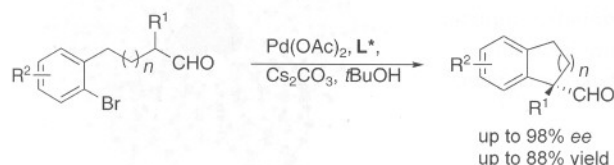


An enhanced performance: Electroluminescent devices incorporating a simple carbazole/oxadiazole hybrid as a host for dopants show maximum external quantum efficiencies (η_{EQE}) as high as 20.2% for green and 18.5% for deep red electrophosphorescence (see picture, J = current density). The host can be conveniently prepared and has good thermal and morphological stabilities and a high triplet energy level.

Electrophosphorescence

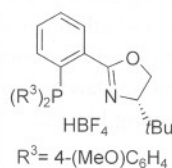
Y. Tao, Q. Wang, C. Yang,* Q. Wang, Z. Zhang, T. Zou, J. Qin, D. Ma* 8104–8107

A Simple Carbazole/Oxadiazole Hybrid Molecule: An Excellent Bipolar Host for Green and Red Phosphorescent OLEDs



Phoxy ligand: The first catalytic method for the asymmetric palladium-catalyzed intramolecular α -arylation of α -branched aldehydes was developed (see scheme).

This process is distinguished by the high yields and enantioselectivities that can be obtained, making this protocol a useful synthetic tool for further applications.



Asymmetric Catalysis

J. García-Fortanet, S. L. Buchwald* 8108–8111

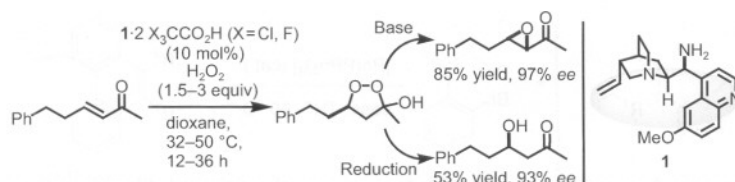
Asymmetric Palladium-Catalyzed Intramolecular α -Arylation of Aldehydes

Asymmetric Epoxidation

C. M. Reisinger, X. Wang,
B. List* — 8112–8115



Catalytic Asymmetric Hydroperoxidation of α,β -Unsaturated Ketones: An Approach to Enantiopure Peroxyhemiketals, Epoxides, and Aldols



Efficient, selective: The primary amine salt **1** derived from quinine efficiently catalyzes the highly enantioselective hydroperoxidation of α,β -unsaturated ketones furnishing stable and isolable cyclic peroxyhemiketals in enantiopure

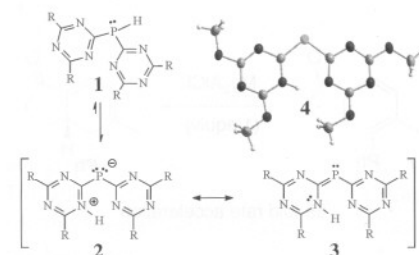
form. The versatility of the peroxyhemiketals was demonstrated with the syntheses of aldols and epoxides from α,β -unsaturated ketones and hydrogen peroxide (see scheme).

Triazinyl Phosphorus Compounds

B. Hoge,* W. Wiebe — 8116–8119

The Influence of Electron-Withdrawing Groups on the Chemistry of Phosphorus: Tautomerization of Bis(*s*-triazinyl)-phosphanes

A one-sided deal: The bis(*s*-triazin-2-yl)phosphane derivative **1** exhibits a solvent- and temperature-dependent equilibrium with its zwitterionic tautomer **2**. The significantly different P–C bond lengths in the methoxy derivative **4** (174.5/ 179.4 pm; red O, blue N, green P) can be described by the formulation of a mesomeric phosphalkene derivative **3**. R = OCH₃, *i*Pr.

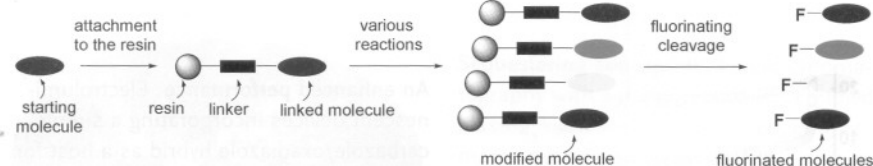


Synthetic Methods

M. S. Wiehn, S. D. Lindell,
S. Bräse* — 8120–8122



Fluorinating Cleavage of Solid Phase Linkers for Combinatorial Synthesis



Multitasking: A new preparative route to fluorine-containing compounds combines the advantages of solid-phase synthesis with the incorporation of fluorine at the end of the synthetic route. A sulfur linker enables simultaneous fluorination of the

target structures in the cleavage step. As it is stable under different reaction conditions, the linker has potential in the combinatorial synthesis of fluorinated drug structures.

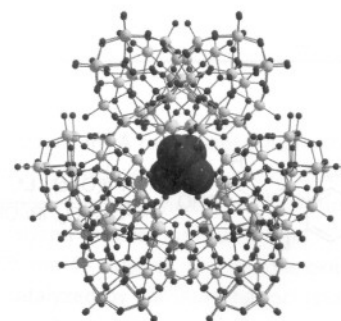
Template Synthesis

X. Fang, P. Kögerler* — 8123–8126



PO₄³⁻-Mediated Polyoxometalate Supercluster Assembly

Small anion, big task: The assembly of a ten-component, heterochiral polyoxo-metalate aggregate, driven by the templating effect of a single phosphate anion, proceeds through a coordination-number-controlled formation route from three dimeric Dawson anion based magnetic building blocks.



Supporting information is available on www.angewandte.org (see article for access details).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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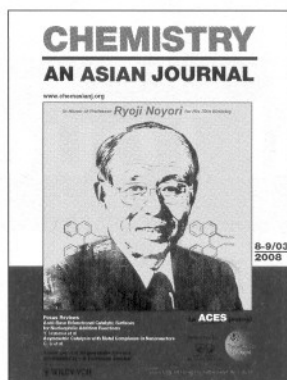
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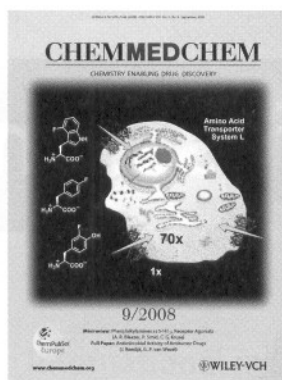
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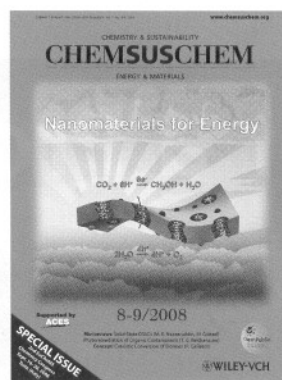
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