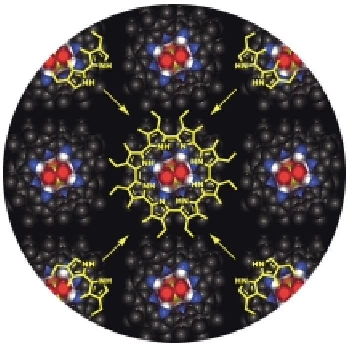
ANGEWANDTE
CHEMIE
A Journal of the
Gesellschaft
Deutscher Chemiker
INTERNATIONAL EDITION
2002
41/8
Pages 1255 – 1446

COVER PICTURE

The cover picture shows the simple, one-step synthesis of cyclo[8]pyrroles, a new class of aromatic heteroannulene. Using a newly developed biphasic oxidative coupling procedure that employs aqueous $FeCl_3$ as the oxidant, these novel porphyrin-like systems may be obtained in yields exceeding 70% starting from well-known bipyrrolic precursors. While formally derived from porphyrin as the result of substituting a pyrrole for each of the original bridging *meso*-carbon atoms, the cyclo[8]pyrroles differ from these quintessential tetrapyrrolic macroycles by virtue of Q-like absorption bands that are red-shifted into the near IR. Cyclo[8]pyrroles also show a propensity for protonation and anion binding that is underscored by the X-ray structure of the sulfate salt that makes up the background for this illustration. More on these exciting new molecules can be found in the communication by J. L. Sessler et al. on pp. 1422 – 1425.

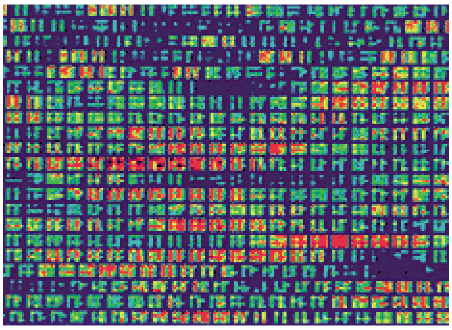


REVIEWS

Contents

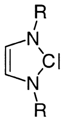
Increasingly important elements of postgenomic biological research are DNA microarrays or DNA chips (see picture). Chemistry has made and should continue to make key contributions to the manufacture and application of these microarrays. This review covers current methods in DNA array production.

Angew. Chem. **2002**, *114*, 1326 – 1341



Keywords: analytical methods · combinatorial chemistry · DNA microarrays · nucleotides · surface analysis

Universal ligands: N-Heterocyclic carbenes such as **A** – **D** have become universal ligands in organometallic and inorganic coordination chemistry. C–H activation, C–C, C–H, C–O, and C–N bond formation are examples of catalytic processes, in which the established ligand class, the organophosphanes, will be supplemented and, in part, replaced by N-heterocyclic carbenes (especially of type **A**) in the new generation of organometallic catalysts to come.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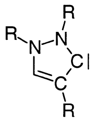
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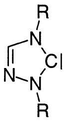
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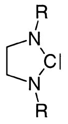
D

Angew. Chem. **2002**, *114*, 1342 – 1363

W. A. Herrmann* .... 1290 – 1309

N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis

Keywords: carbene ligands · carbenes · heterocycles · homogeneous catalysis

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Under the keywords flee, collaborate, and forget the effects of National Socialism on chemistry and biochemistry in universities and Kaiser Wilhelm Institutes are presented. At the center lies the dismissal and enforced emigration of all Jewish chemists and biochemists and a few of their non-Jewish colleagues, who were identified as critics of the regime or "Friends of Jews", the different forms of collaboration of the remaining scientists, the isolated cases of nonconformity, and the general silence of German chemists after 1945—their effort to let the 12-year National Socialist rule and their share of the responsibility to be forgotten.

Angew. Chem. **2002**, *114*, 1364 – 1383

U. Deichmann* .... 1310 – 1328

Chemists and Biochemists during the National Socialist Era

Keywords: antisemitism · emigration · history of chemistry · science policy

MINIREVIEW

Perfectly branched: dendritic polymers have become increasingly important tools in medical diagnostics and therapy (see picture). In particular, progress has been made in diagnostics, especially in biosensors and by using dendrimers with Gd complexes in magnetic resonance imaging (MRI). Dendrimers also show promising therapeutic properties, with potential applications in gene transfection, in drug-delivery systems, and in neutron-capture therapy.

Angew. Chem. **2002**, *114*, 1385 – 1390

S.-E. Stiriba, H. Frey,*
R. Haag* .... 1329 – 1334

Dendritic Polymers in Biomedical Applications: From Potential to Clinical Use in Diagnostics and Therapy

Keywords: biosensors · dendritic polymers · gene transfection · medicinal chemistry · MRI

VIPs

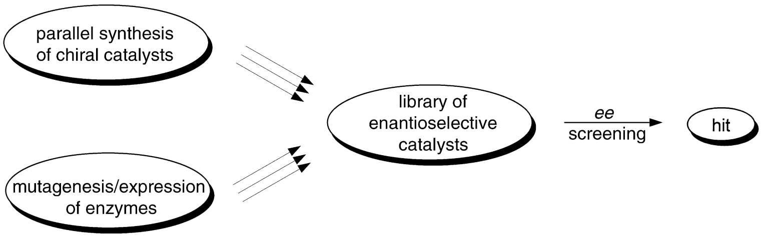
The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.com

Cyclotetrasilenide Ion: A Reversible Redox System of Cyclotetrasilenyl Cation, Radical, and Anion — T. Matsuno, M. Ichinohe, A. Sekiguchi* ◆

Synthesis and Structure of Na_3N — D. Fischer, M. Jansen*

HIGHLIGHT

Combinatorial asymmetric catalysis and the directed evolution of enantioselective enzymes requires rapid high-throughput screening systems for assaying the *ee* value of large numbers of samples (see picture). Three new approaches are reviewed, which are based on DNA microarrays, enzymatic methods, and enzyme immunoassays.



Angew. Chem. **2002**, *114*, 1391 – 1394

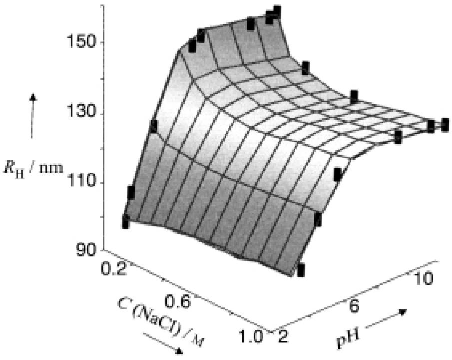
M. T. Reetz* . . . . 1335 – 1338

New Methods for the High-Throughput Screening of Enantioselective Catalysts and Biocatalysts

Keywords: asymmetric catalysis · combinatorial chemistry · DNA microarrays · enzyme immunoassay · high-throughput screening

COMMUNICATIONS

Polypeptide secondary structure controls the dimensions of aggregates formed from a polybutadiene-*b*-poly(L-glutamic acid) diblock copolymer after direct dissolution into water. The hydrodynamic radius (R_H) of these aggregates (even at high NaCl concentrations) were found to correlate (see picture) with a transition from a compactly folded α-helical poly(L-glutamic acid) block at low pH to an extended random coil conformation at basic pH.



Angew. Chem. **2002**, *114*, 1395 – 1399

F. Chécot, S. Lecommandoux,*
Y. Gnanou, H.-A. Klok* . . . . 1339 – 1343

Water-Soluble Stimuli-Responsive Vesicles from Peptide-Based Diblock Copolymers

Keywords: amino acids · copolymers · nanostructures · self-assembly · vesicles

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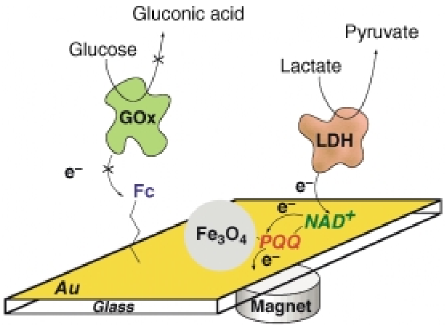
Sugar and magnetism: The selective analysis of glucose and lactate in a mixture was achieved by the application of glucose oxidase (GOx) and lactate dehydrogenase (LDH) using a ferrocene (Fc) monolayer-functionalized electrode, catalyst–NAD$^+$-functionalized magnetic particles, and an external magnetic field (see schematic representation).



Angew. Chem. **2002**, *114*, 1399 – 1402

E. Katz, L. Sheeney-Haj-Ichia,
A. F. Bückmann, I. Willner* 1343 – 1346

Dual Biosensing by Magneto-Controlled Bioelectrocatalysis

Keywords: colloids · cyclic voltammetry · electrochemistry · magnetic particles · sensors

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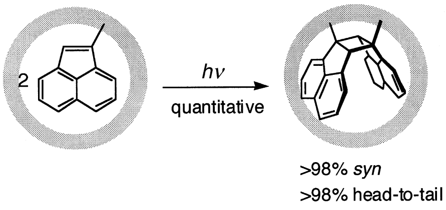
Molecular flasks of self-assembled M_6L_4 nanocages promote the [2+2] photodimerization of olefins in a surprisingly efficient fashion. Thus, the dimerization of acenaphthylenes and naphthoquinones quantitatively proceeded in the cavity with remarkable rate acceleration and perfect regio- and stereocontrol (> 98 %, see scheme).

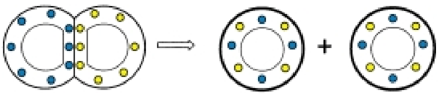


Angew. Chem. **2002**, *114*, 1403 – 1405

M. Yoshizawa, Y. Takeyama,
T. Kusukawa, M. Fujita* . . . . 1347 – 1349

Cavity-Directed, Highly Stereoselective [2+2] Photodimerization of Olefins within Self-Assembled Coordination Cages

Keywords: dimerization · palladium · photochemistry · regioselectivity · self-assembly



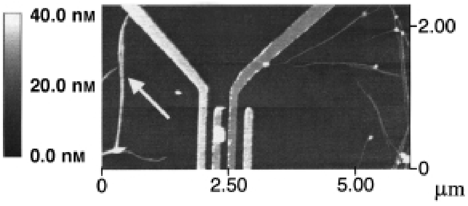
Stickiness of giant vesicles, visible under the light microscope, can be promoted or prevented (see figure) by substances such as poly-L-lysine (cationic), polyvinylpyrrolidone (nonionic; yellow), and heparin (anionic; blue). In one particular system, adhesion was time-dependent owing to exchange of components by a pair of electrostatically adhered vesicles.

Angew. Chem. **2002**, *114*, 1406 – 1408

F. M. Menger,* V. A. Seredyuk,
A. A. Yaroslavov .... 1350 – 1352

Adhesive and Anti-Adhesive Agents in Giant Vesicles

Keywords: adhesion • heparin • membranes • vesicles



Combination of nanolithography and electrochemistry allows the chemical modification of individual single-walled carbon nanotubes (SWCNTs) by attachment of functional groups. This approach allows both the reductive as well as oxidative coupling of substituted phenyl groups, presumably to defect sites in the tubes. The thickness of the deposited layer can be controlled by the duration of the potential applied. The picture shows an atomic force micrograph of SWCNTs after the reductive coupling of a 4-nitrophenyl diazonium salt.

Angew. Chem. **2002**, *114*, 1409 – 1411

S. E. Kooi, U. Schlecht, M. Burghard,*
K. Kern .... 1353 – 1355

Electrochemical Modification of Single Carbon Nanotubes

Keywords: electrochemistry • nanotubes • oxidation • reduction • surface chemistry

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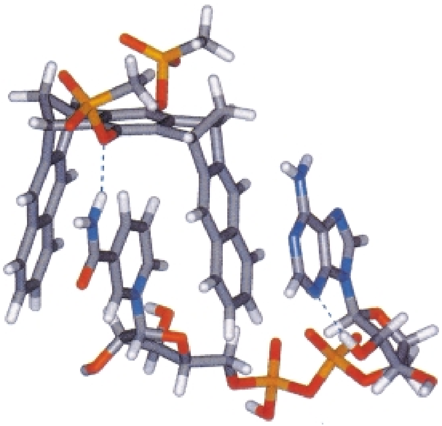

A molecular clip made of two naphthalene side walls and bisphosphonate arms selectively binds to *N*-alkylpyridinium ions in water. Through the unique potential of this clip to combine π – cation and electrostatic interactions with the hydrophobic effect, the host molecule is able to complex NAD$^+$ (nicotinamide adenine dinucleotide; see picture) efficiently in aqueous solution.

Angew. Chem. **2002**, *114*, 1411 – 1415

C. Jasper, T. Schrader,* J. Panitzky,
F.-G. Klärner* .... 1355 – 1358

Selective Complexation of *N*-Alkylpyridinium Salts: Recognition of NAD$^+$ in Water

Keywords: molecular clips • molecular recognition • NAD • *N*-alkylpyridinium salts • noncovalent interactions

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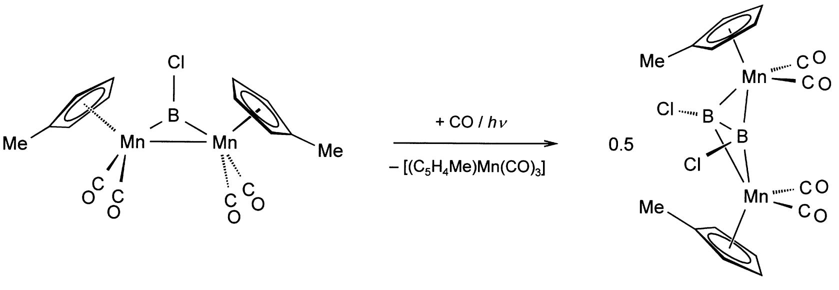
Boron, butterflies, and the missing link: The first synthetic link between electron-precise borylene complexes such as **1** and electron-deficient metallaboranes is achieved with the preparation of **2**. This result introduces two novel features to the chemistry of the metallaboranes—unbridged B_2Hal_2 moieties (Hal = halogen) as cluster fragments and the four vertex *nido*-"butterfly" as a structural motif.



1 **2**

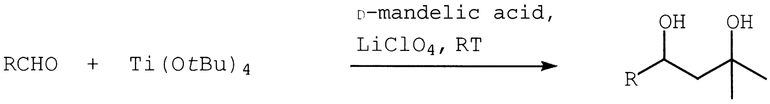
Angew. Chem. **2002**, *114*, 1415 – 1417

H. Braunschweig,* M. Colling, C. Hu,
K. Radacki .... 1359 – 1361

From Classical to Nonclassical Metal – Boron Bonds: Synthesis of a Novel Metallaborane

Keywords: boron • borylene complexes • manganese • metallaboranes • metal – boron bonds

Mobile hydrogen atoms: The hydrogen atoms of tertiary butyl groups are significantly more mobile than is generally assumed. Under very mild and acidic conditions aldehydes react with Ti(O*t*Bu)$_4$ to form diols in the presence of LiClO$_4$ and α-hydroxy acid (see scheme).



Angew. Chem. **2002**, *114*, 1423 – 1425

R. Mahrwald* .... 1361 – 1363

Enantioselective C–C Bond Formation with Titanium(IV) Alkoxides—an Unusual Alkylation

Keywords: aldehydes • alkylation • C–H activation • enantioselectivity • titanium

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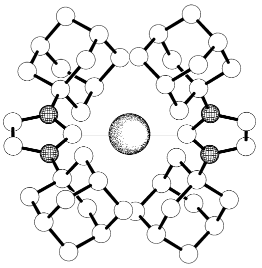
Highly active but sterically demanding: Ambient-temperature Suzuki cross-coupling of aryl chlorides is possible with a palladium(0) complex bearing two bulky, N-heterocyclic carbene ligands (see structure). Nearly quantitative yields are obtained within two hours with some reagents, which makes this compound the most active catalyst known to date under these conditions.



Angew. Chem. **2002**, *114*, 1421 – 1423

C. W. K. Gstöttmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche, W. A. Herrmann* .... 1363 – 1365

A Defined N-Heterocyclic Carbene Complex for the Palladium-Catalyzed Suzuki Cross-Coupling of Aryl Chlorides at Ambient Temperatures

Keywords: carbenes • carbene ligands • C–C coupling • homogeneous catalysis • palladium

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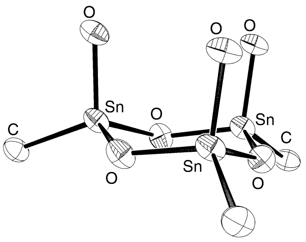
An eighty-year-old question answered: The basic structural element of monoorganotin acids (see structure) is formed by *cyclo*-tristannoxanes in a chairlike conformation with ligands bonded to the Sn$_3$O$_3$ heterocycle in equatorial positions. The three axial hydroxy groups display a *cis* arrangement. Thus the fundamental structural element of this class of compounds is elucidated.



Angew. Chem. **2002**, *114*, 1425 – 1427

J. Janssen, J. Magull, H. W. Roesky* .... 1365 – 1367

X-Ray Structural Characterization of a Monoorganotin Acid

Keywords: chlorine • hydrolysis • monorganotin acids • structure elucidation • tin

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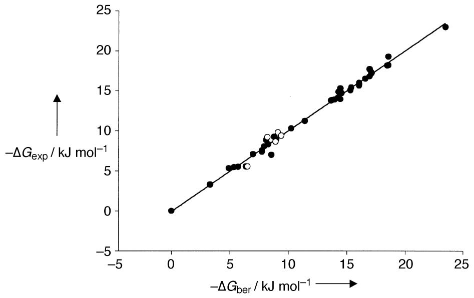
Energy increments for van der Waal effects are determined by bond-energy measurements on over 50 guest compounds (see diagram) and can be used for prediction. Hydrophobic effects can be discounted on the basis of comparison measurements with alkylated derivatives.



Angew. Chem. **2002**, *114*, 1418 – 1420

T. Liu, H.-J. Schneider* ..... 1368 – 1370

Additivity and Quantification of Dispersive Interactions—from Cyclopropyl to Nitro Groups: Measurements on Porphyrin Derivatives

Keywords: bond energy • noncovalent interactions • porphyrinoids • solvent effects • supramolecular chemistry

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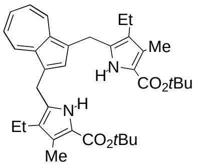
A back-to-front synthesis of azuliporphyrins from an azulitripyrrane (**1**) has been developed. This methodology has allowed the first rational synthesis of the dicarbaporphyrinoid system **2**.



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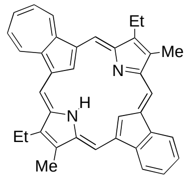


2

Angew. Chem. **2002**, *114*, 1429 – 1432

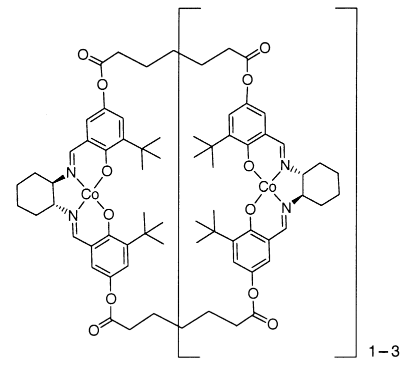
S. R. Graham, D. A. Colby, T. D. Lash* .... 1371 – 1374

An Azulene Analogue of the Tripyrranes and Carbaporphyrinoids Therefrom

Keywords: aromaticity • azulene • nitrogen heterocycles • porphyrinoids

Prepared by a high yield, chromatography-free route, “oligosalen” exists as a mixture of dimer, trimer, and tetramer (see picture). Derived catalyst systems display remarkable activity and selectivity in the asymmetric ring-opening of epoxides, with turnover numbers exceeding 100000 in some cases.

Angew. Chem. **2002**, *114*, 1432 – 1435



J. M. Ready, E. N. Jacobsen* 1374 – 1377

A Practical Oligomeric [(salen)Co] Catalyst for Asymmetric Epoxide Ring-Opening Reactions

Keywords: asymmetric catalysis · epoxides · homogeneous catalysis · kinetic resolution · N,O ligands

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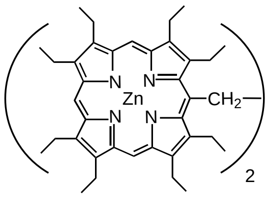
Supramolecular chirality induction and inversion processes can be controlled by phase transition. The achiral *syn* (face-to-face) conformer of the ethane-bridged bis(zinc octaethylporphyrin) (see figure) interacts with enantiopure monoamines in solution and solid-state phases to yield the corresponding *anti* conformer. The chirality sign in the solid state is opposite to that in solution because of the formation of an aggregated species with inverted intermolecular helicity.

Angew. Chem. **2002**, *114*, 1436 – 1439



V. V. Borovkov,* T. Harada, Y. Inoue, R. Kuroda* .... 1378 – 1381

Phase-Sensitive Supramolecular Chirogenesis in Bisporphyrin Systems

Keywords: chirality · circular dichroism · porphyrinoids · solid-state structures · supramolecular chemistry · zinc

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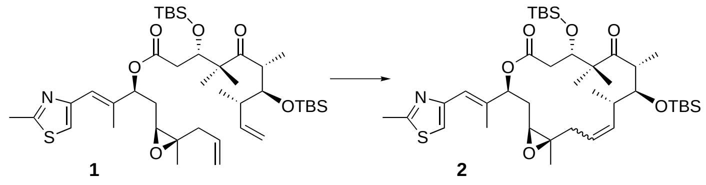
A stereoselective synthesis of epothilone B was achieved by the metathesis of the diene **1**, by use of a new Grubbs catalyst to form the C9–C10 bond, followed by hydrogenation and deprotection of **2**; TBS = *tert*-butyldimethylsilyl.



Angew. Chem. **2002**, *114*, 1439 – 1441

J. Sun, S. C. Sinha* .... 1381 – 1383

Stereoselective Total Synthesis of Epothilones by the Metathesis Approach Involving C9–C10 Bond Formation

Keywords: asymmetric catalysis · epothilones · metathesis · natural products · total synthesis

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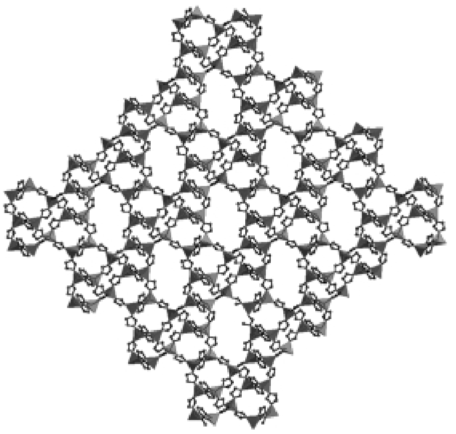
A highly robust metal-organic zeotype was created by expansion of the zeolite topology. The novel nanoporous material $[Co_5(im)_{10}\cdot 2MB]_\infty$ (see structure) exhibits not only a zeolite-like topology, but also the chemically functionalizable properties of zeolites; im = imidazole, MB = 3-methyl-1-butanol.

Angew. Chem. **2002**, *114*, 1442 – 1444



Y.-Q. Tian, C.-X. Cai, Y. Ji, X.-Z. You,* S.-M. Peng, G.-H. Lee ...... 1384 – 1386

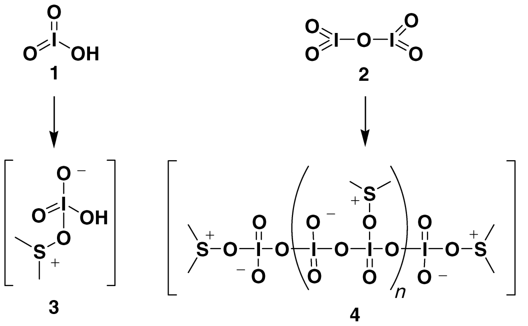
$[Co_5(im)_{10}\cdot 2MB]_\infty$: A Metal-Organic Open-Framework with Zeolite-Like Topology

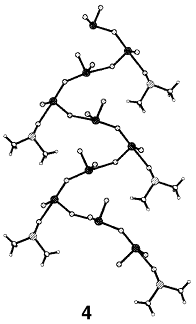
Keywords: cobalt · coordination polymer · crystal engineering · nitrogen heterocycles · zeolite analogues

K. C. Nicolaou,* T. Montagnon,
P. S. Baran 1386–1389

HIO_3 and I_2O_5: Mild and Selective Alternative Reagents to IBX for the Dehydrogenation of Aldehydes and Ketones

Economic and convenient: Iodic acid (**1**) and iodine pentoxide (**2**) form complexes **3** and **4**, respectively, with DMSO when heated at 80°C for 1 h. The complexes are efficient agents for the dehydrogenation of ketones and aldehydes at 45–65°C. X-ray crystallographic analysis (see picture) shows that the iodine pentoxide · DMSO complex **4** self-assembles into a remarkable helix in the solid state.

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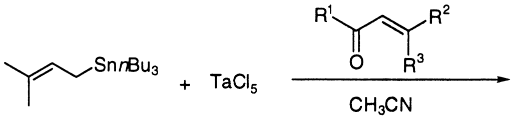
Angew. Chem. **2002**, *114*, 1444–1447

Keywords: dehydrogenation · enones · hypervalent compounds · iodine · synthetic methods

I. Shibata,* T. Kano, N. Kanazawa,
S. Fukuoka, A. Baba 1389–1392

Generation of Organotantalum Reagents and Conjugate Addition to Enones

A superior method of conjugate allylation: The transmetalation of allyltin compounds with $TaCl_5$ yielded active tantalum reagents for conjugate addition to enones. Even bulky allyl moieties could be introduced to enones in this manner (see scheme). Both cyclic and acyclic enones reacted facilely under extremely mild conditions.

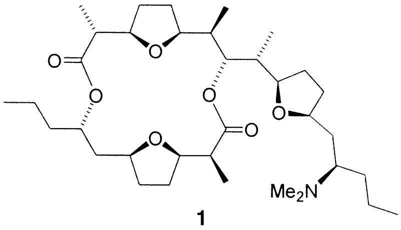


Angew. Chem. **2002**, *114*, 1447–1450

Keywords: allylation · Michael addition · synthetic methods · tantalum · tin · transmetalation

S. H. Kang,* J. W. Jeong, Y. S. Hwang,
S. B. Lee 1392–1395

Total Synthesis of (+)-Pamamycin-607



1

Complete stereoselectivity was observed in the total synthesis of pamamycin-607 (**1**), which proceeded by iodoetherification of γ-triethylsilyloxyalkenes in the presence of an essential additive, silver carbonate, to provide the requisite three *cis*-2,5-disubstituted tetrahydrofuran units. Other key functionalization includes cuprate addition to epoxide, olefinations, Paterson aldol condensation, Evans *anti* reduction, and macrolactonization.

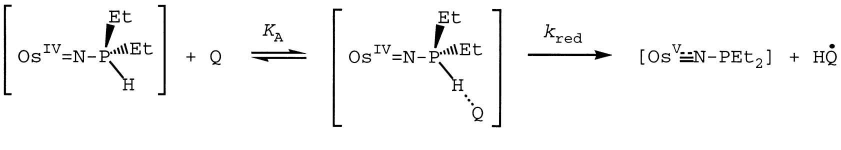
Angew. Chem. **2002**, *114*, 1450–1453

Keywords: asymmetric synthesis · cyclization · natural products · pamamycin · total synthesis

M. H. V. Huynh,*
T. J. Meyer* 1395–1398

Proton-Coupled Electron Transfer from Phosphorus: A P–H/P–D Kinetic Isotope Effect of 178

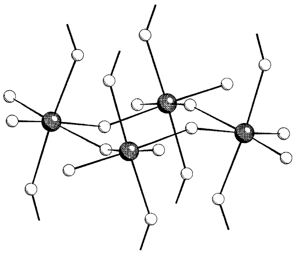
Remote from the metal: The first example of proton-coupled electron transfer involving a phosphorus atom that is not directly bonded to a metal center (shown schematically; Q = benzoquinone) occurs with an osmium–phosphoraniminato complex. The large magnitude of the kinetic isotope effect is remarkable and opens the possibility of observing giant isotope effects in related reactions where proton-coupled electron transfer is the dominant mechanism.


$$\left[\mathrm{Os^{IV}{=}N{-}P(Et)_2H}\right] + Q \overset{K_A}{\rightleftharpoons} \left[\mathrm{Os^{IV}{=}N{-}P(Et)_2H\cdots Q}\right] \xrightarrow{k_{red}} [\mathrm{Os^{V}{\equiv}N{-}PEt_2}] + H\dot{Q}$$

Angew. Chem. **2002**, *114*, 1453–1456

Keywords: electron transfer · isotope effects · kinetics · osmium · P ligands · reduction

Slow thermal decomposition of CrF_5 at 403 K affords a new crystal modification of CrF_4. The basic units in the crystal structure of this β-CrF_4 are tetrameric rings formed by four corner-sharing CrF_6 octahedra (see picture), which are linked together to form isolated columns running along the *c* axis.



Angew. Chem. **2002**, *114*, 1456 – 1457

P. Benkič, Z. Mazej,*
B. Žemva . . . . 1398 – 1399

A New Crystal Modification of Chromium Tetrafluoride: β-CrF_4

Keywords: chromium · fluorides · solid-state reactions · structure elucidation

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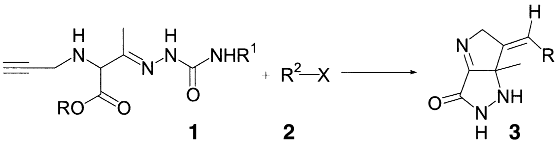
Stereoselective dominos: Cascade reactions of easily accessible α-propargylaminohydrazones **1** represent a simple and efficient method for the preparation of pyrazolones **3**.



Angew. Chem. **2002**, *114*, 1458 – 1460

E. Rossi,* A. Arcadi,* G. Abbiati,
O. A. Attanasi,
L. De Crescentini . . . . 1400 – 1402

Sequential Base-Promoted Annulation/Palladium-Catalyzed Domino 1,5-Enyne Arylation and Vinylation of α-Propargylaminohydrazones

Keywords: annulation · cyclization · domino reactions · nitrogen heterocycles · palladium

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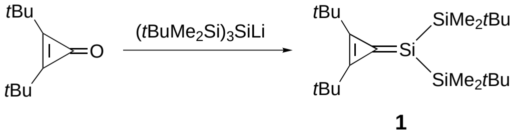
Unique structural characteristics and reactivities caused by the less-polar Si–C double bond in the 4-silatriafulvene **1** were revealed by spectroscopic studies and X-ray structural analysis. Compound **1** was isolated by applying a synthetic procedure using a sila-Peterson-type reaction.



Angew. Chem. **2002**, *114*, 1460 – 1462

K. Sakamoto,* J. Ogasawara, Y. Kon,
T. Sunagawa, C. Kabuto,
M. Kira* . . . . 1402 – 1404

The First Isolable 4-Silatriafulvene

Keywords: aromaticity · electronic structure · silene · silicon

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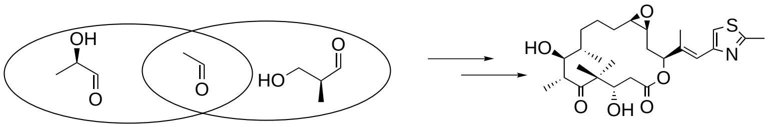
Enzymatic reactions catalyzed by DERA provide the basis for a new strategy for the synthesis of novel pyranose synthons. The utility of this very convergent and effective method is demonstrated by the concise total synthesis of epothilones (see scheme; DERA = 2-deoxyribose-5-phosphate aldolase).



Epothilone A

Angew. Chem. **2002**, *114*, 1462 – 1465

J. Liu, C.-H. Wong* . . . . 1404 – 1407

Aldolase-Catalyzed Asymmetric Synthesis of Novel Pyranose Synthons as a New Entry to Heterocycles and Epothilones

Keywords: aldol reaction · enzyme catalysis · epothilones · synthetic methods · total synthesis

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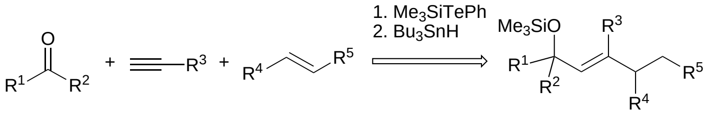
The domino, sequential coupling reaction provides a convergent and stereoselective synthetic route for allylic alcohols from carbonyl compounds, alkynes, and alkenes (see scheme). The reaction involves sequential radical coupling reactions initiated by the α-siloxy radicals, which are generated from carbonyl compounds and silyl tellurides.



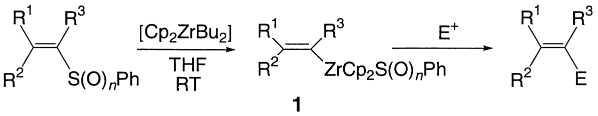
Angew. Chem. **2002**, *114*, 1465 – 1467

S. Yamago,* M. Miyoshi, H. Miyazoe,
J. Yoshida* . . . . 1407 – 1409

Convergent Synthesis of Silylated Allylic Alcohols by a Stereoselective Domino, Sequential Radical-Coupling Reaction

Keywords: C–C coupling · domino reactions · multicomponent reactions · radical reactions · synthetic methods

A transformation with promising versatility: The vinyl zirconium complex **1** can be prepared readily in situ from the educts mentioned in the title and reacts with electrophiles, including other transition metal complexes, to give polysubstituted olefins (see scheme; $n = 0-2$, $Cp = C_5H_5$). A five-membered zirconacycle en route to the vinyl complex apparently isomerizes to give the stable *E* isomer before elimination.



Angew. Chem. **2002**, *114*, 1468 – 1471

S. Farhat, I. Marek* .... 1410 – 1413

From Vinyl Sulfides, Sulfoxides, and Sulfones to Vinyl Transition Metal Complexes

Keywords: elimination · isomerization · sulfur · transmetalation · zirconium

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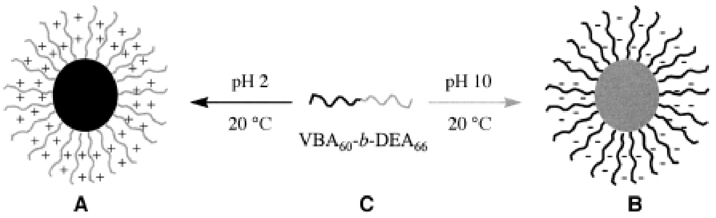
Schizophrenic character: A novel zwitterionic AB diblock copolymer was prepared by atom-transfer radical polymerization (ATRP) of 2-(diethylamino)-ethyl methacrylate (DEA) and 4-vinyl benzoic acid (VBA). Both conventional micelles and inverted micelles can be formed in aqueous solution at ambient temperature, by controlling the solution pH. At low pH, VBA-core micelles (**A**) are formed, at high pH DEA-core micelles (**B**) are formed, and at neutral pH, the system precipitates (**C**; see figure).



Angew. Chem. **2002**, *114*, 1471 – 1474

S. Liu, S. P. Armes* .... 1413 – 1416

Polymeric Surfactants for the New Millennium: A pH-Responsive, Zwitterionic, Schizophrenic Diblock Copolymer

Keywords: block copolymers · micelles · polymerization · self-assembly · surfactants

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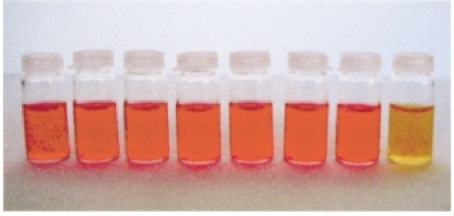
Nitrate sensing: A selective colorimetric sensing of nitrate by a mercury complex of an oxa-thia-aza macrocycle functionalized with an azo dye is described. The figure shows the color of acetonitrile solutions of the mercury complex in the presence of the following species: from left to right, no anion, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, and NO_3^-.



Angew. Chem. **2002**, *114*, 1474 – 1477

F. Sancenón, R. Martínez-Máñez,*
J. Soto .... 1416 – 1419

A Selective Chromogenic Reagent for Nitrate

Keywords: azo compounds · chromophores · mercury · nitrates · sensors

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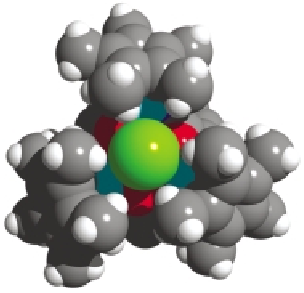
A redox-responsive receptor based on a self-assembled metallamacrocycle is able to selectively bind molecular LiF (see X-ray crystal structure) and act as a highly selective chemosensor for the detection of fluoride anions by electrochemical means, even in protic solvents.



Angew. Chem. **2002**, *114*, 1477 – 1480

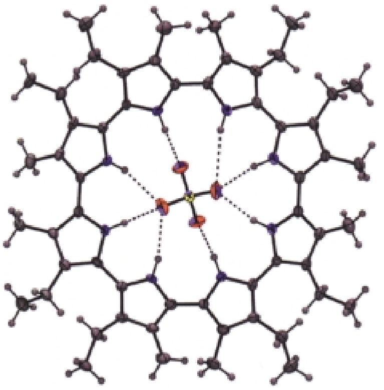
M.-L. Lehaire, R. Scopelliti,
H. Piotrowski, K. Severin* .. 1419 – 1422

Selective Recognition of Fluoride Anion Using a Li^+ – Metallacrown Complex

Keywords: fluorides · lithium · metallacycles · receptors · supramolecular chemistry

Easily obtained in a single step from bipyrrolic precursors in yields over 70%, cyclo[8]pyrroles represent a new class of porphyrin analogues that display the classic disklike structure of porphyrins. The X-ray crystal structure of one of the cyclo[8]pyrroles obtained (see picture) shows that the macrocycle acts as a formal diprotonated receptor and forms eight hydrogen bonds to a sulfate ion bound within its core.

Angew. Chem. **2002**, *114*, 1480–1483



D. Seidel, V. Lynch,
J. L. Sessler* 1422–1425

Cyclo[8]pyrrole: A Simple-to-Make Expanded Porphyrin with No Meso Bridges

Keywords: anions · aromaticity · macrocycles · oxidative coupling · porphyrinoids

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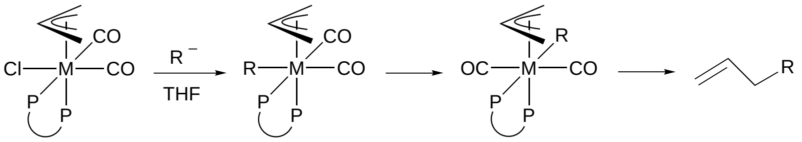
A *cis*-to-*trans* isomerization of the initially formed product is a key step following the nucleophilic attack of acetylide, alkyl, and enolate carbanions at the metal center of [MCl(η^3-C_3H_5)(CO)$_2$(dmpm)] complexes (M = Mo, W; dmpm = bis(dimethylphosphanyl)methane ($\widehat{PP}$); see scheme). Subsequent metal-to-allyl migration followed by elimination yields the corresponding coupling products.



Angew. Chem. **2002**, *114*, 1485–1487

J. Pérez,* V. Riera, A. Rodríguez,
S. García-Granda 1427–1429

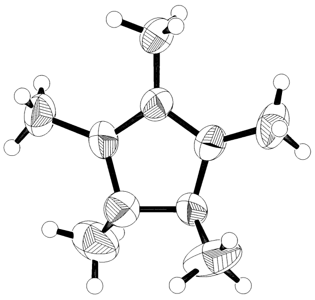
C–C Coupling between an η^3-Allyl Ligand and Carbon Nucleophiles in Molybdenum and Tungsten Complexes: Structural Characterization of the Key Intermediate

Keywords: allylation · allylic compounds · molybdenum · tungsten

---

More than 100 years after the cyclopentadienyl anion appeared in the literature, the first cyclopentadienyl cation, the pentamethyl derivative $C_5Me_5^+$, has now been prepared in a single step as the tetrakis(pentafluorophenyl)borate salt. This material is crystalline and stable at room temperature for weeks. The crystal structure of $C_5Me_5^+$ (see picture) reveals localized bonding.

Angew. Chem. **2002**, *114*, 1487–1489



J. B. Lambert,* L. Lin,
V. Rassolov 1429–1431

The Stable Pentamethylcyclopentadienyl Cation

Keywords: antiaromaticity · aromaticity · carbocations · structure elucidation

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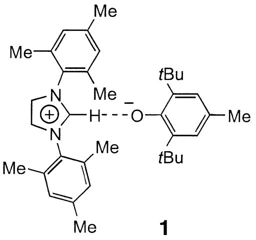
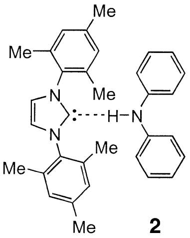
Two unprecedented hydrogen bonds were observed in the adducts obtained by the reactions of an N-heterocyclic carbene with a bulky phenol and with diphenylamine. In the former case, proton transfer yields an imidazolium aryloxide (**1**) containing the shortest C–H ··· O interaction seen to date and in the latter, the hydrogen atom remains bound to the organic acid but forms a unique N–H ··· C hydrogen bond (**2**).

Angew. Chem. **2002**, *114*, 1490–1492



1



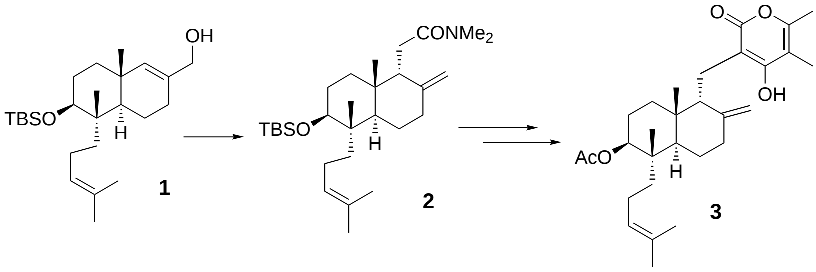
2

J. A. Cowan, J. A. C. Clyburne,*
M. G. Davidson,* R. L. W. Harris,
J. A. K. Howard, P. Küpper, M. A. Leech,
S. P. Richards 1432–1434

On the Interaction between N-Heterocyclic Carbenes and Organic Acids: Structural Authentication of the First N–H ··· C Hydrogen Bond and Remarkably Short C–H ··· O Interactions

Keywords: carbenes · hydrogen bonds · pi interactions · structure elucidation

The key step in the total synthesis of sesquicillin (**3**) is a stereoselective Claisen rearrangement of **1** to afford **2**. The synthesis also features an efficient sequence to install an α-pyrone moiety in a hindered environment; TBS = *tert*-butyldimethylsilyl.



Angew. Chem. **2002**, *114*, 1492 – 1495

F. Zhang, S. J. Danishefsky* . 1434 – 1437

An Efficient Stereoselective Total Synthesis of DL-Sesquicillin, a Glucocorticoid Antagonist

Keywords: aldol reaction · lactones · sigmatropic rearrangement · steric hindrance · total synthesis

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

Accelerated publications

* Author to whom correspondence should be addressed

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