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. Filser, D. Kowalczyk, C. Jones, M. Wild, U. Ipe, D. Vestweber, H. Kunz**
Synthetic Glycopeptides with Varied Sialyl Lewis^x Structures as Cell-Adhesion Ligands for E-Selectin

*J. Glöckler, S. Klützke, W. Meyer-Zaika, A. Reller, F. J. García-García, Hans-H. Strehblow, P. Keller, E. Rentschler, W. Kläui**
Towards Nanostructured Water-Soluble and Catalytically Active Rhodium Clusters

R. Fischer, M. Gärtner, H. Görls, L. Yu, M. Reiher, M. Westerhausen**
Synthesis and Properties of the THF Solvates of Extremely Soluble Bis(2,4,6-trimethylphenyl)calcium and Tris(2,6-dimethoxyphenyl)dicalcium Iodide

*J. Garcia-Álvarez, A. R. Kennedy, J. Klett, R. E Mulvey**
Alkali-Metal-Mediated Manganation: A Method for Directly Attaching Manganese(II) Centers to Aromatic Frameworks

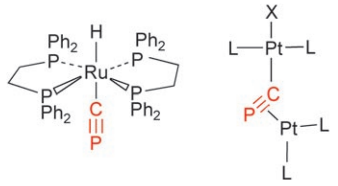
*M. R. Radowski, A. Shukla, H. v. Berlepsch, C. Böttcher, G. Pickaert, H. Rehage, R. Haag**
Supramolecular Aggregates of Dendritic Multishell Architectures as Universal Nanocarriers

C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski, J. Brown*
Highly Efficient, Near-Infrared Electrophosphorescence from a Pt Metalloporphyrin Complex

News

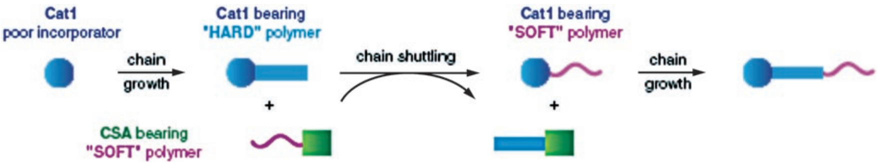
Books

Highlights



An up-and-coming sibling: Unlike the cyanide ion (C≡N$^-$), which is one of the fundamental ions in inorganic chemistry, cyaphide (C≡P$^-$) is not stable unless it is coordinated to a metal center, either as a bridging ligand or, as just recently demonstrated, as a terminal ligand (see scheme; L = monodentate phosphane, X = halide).

C≡P Ligands



Shuttle chain in operation: “Chain-shuttling” polymerization is a promising strategy for the synthesis of high-performance polyolefins. Polymerization takes place block by block using two different catalysts to generate new block copolymers with special properties.

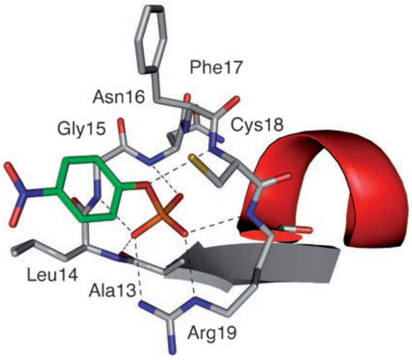
High-Performance Polyolefins

Reviews

Molecular Recognition

A. K. H. Hirsch, F. R. Fischer,
F. Diederich* ______ 338 – 352

Phosphate Recognition in Structural Biology



Filled pockets: The most important interactions involved in biological phosphate recognition have been characterized. From 3003 considered structures, 2456 feature phosphate binding sites (as shown in the picture; ligand skeleton green, C gray, O red, N blue, P orange) without metal ions. The search reveals similarities to phosphate binding by synthetic receptors and points to new approaches for filling phosphate sites in drug-discovery research.

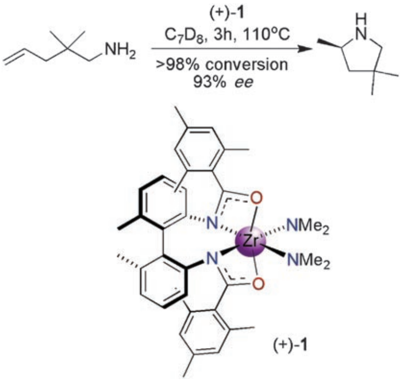
Communications

Asymmetric Catalysis

M. C. Wood, D. C. Leitch, C. S. Yeung,
J. A. Kozak, L. L. Schafer* ______ 354 – 358

Chiral Neutral Zirconium Amidate Complexes for the Asymmetric Hydroamination of Alkenes

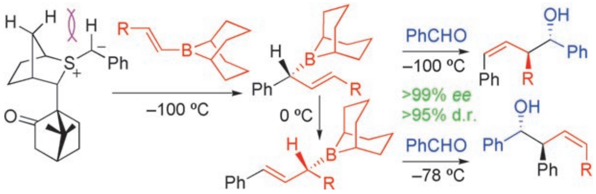
Aminations with amidates: The first C_2-symmetric amidate complexes of zirconium were used for catalytic asymmetric hydroaminations of amino alkenes to prepare chiral *gem*-disubstituted pyrrolidines with up to 93 % *ee* (see scheme). The modular nature of the chiral complexes facilitates their preparation and screening as catalysts.



Allyl boranes

G. Y. Fang, V. K. Aggarwal* ______ 359 – 362

Asymmetric Synthesis of α-Substituted Allyl Boranes and Their Application in the Synthesis of Iso-agatharesinol



Use your borane: A stereocontrolled synthesis of allyl boranes from chiral sulfur ylides and their subsequent reaction with aldehydes to give homoallylic alcohols is described. The allyl boranes also could undergo a stereospecific 1,3-borotropic rearrangement to give another set of homoallylic alcohols (see scheme). The reaction has been applied to an efficient synthesis of iso-agatharesinol.

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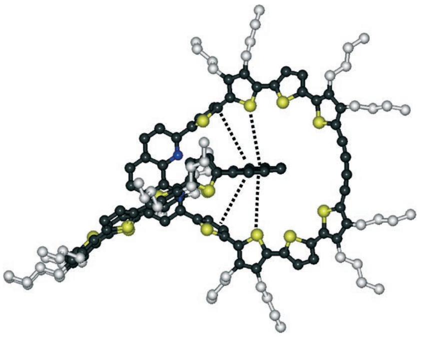


Make it a double: A double metal template strategy has been used to form a “π-conjugated catenane” consisting of intertwined macrocycles with oligothienyl and phenanthroline units (see calculated structure). The optical and redox properties as well as the structural and conformational analyses give clear evidence that the two macrocycles in the catenane influence each other by through-space donor–acceptor interactions.

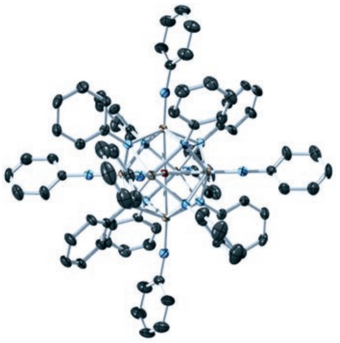
Noncovalent Interactions

P. Bäuerle,* M. Ammann, M. Wilde,
G. Götz, E. Mena-Osteritz, A. Rang,
C. A. Schalley ———— **363 – 368**

Oligothiophene-Based Catenanes: Synthesis and Electronic Properties of a Novel Conjugated Topological Structure

---

A New Class of Metal–Imido Complex: Octahedral hexatantalum clusters $[(ArN)_{14}Ta_6O]$ (see picture; C gray, N blue, O red, Ta orange, Ar = Ph) were formed in good yields by treatment of $[Bn_3Ta{=}N\mathit{t}Bu]$ (Bn = benzyl) or $[Ta(NMe_2)_5]$ with an excess of the appropriate aniline and an equivalent of water. Crystallographic analysis revealed the presence of a central oxygen atom, which was further identified by electrospray mass spectrometry using $^{17}O/^{18}O$-enriched material.



Cluster Compounds

J. L. Krinsky, L. L. Anderson, J. Arnold,*
R. G. Bergman* ———— **369 – 372**

Synthesis and Properties of Oxygen-Centered Tetradecaimido Hexatantalum Clusters

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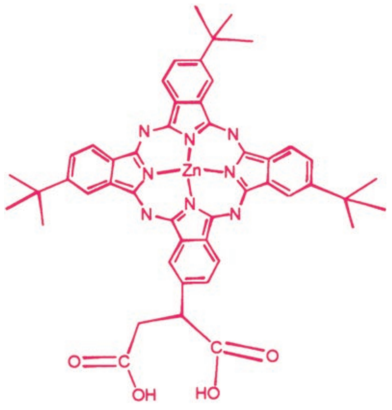

Pushing and pulling by three *tert*-butyl and two carboxylic acid groups, respectively, results in a sensitizer (see picture) that exhibits an incident photon-to-current conversion efficiency of 75 %. A cell sensitized with this compound gives a short-circuit photocurrent density of (6.50 ± 0.20) mA cm^{-2}, an open-circuit voltage of (635 ± 30) mV, and a fill factor of 0.74 ± 0.03, which corresponds to an overall conversion efficiency of 3.05 %.

Solar Cells

P. Y. Reddy, L. Giribabu, C. Lyness,
H. J. Snaith, Ch. Vijaykumar,
M. Chandrasekharam, M. Lakshmikantam,
J.-H. Yum, K. Kalyanasundaram,
M. Grätzel,
M. K. Nazeeruddin* ———— **373 – 376**

Efficient Sensitization of Nanocrystalline TiO$_2$ Films by a Near-IR-Absorbing Unsymmetrical Zinc Phthalocyanine

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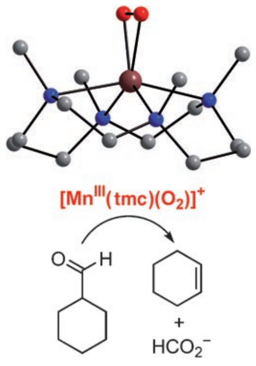


On the side: The crystal structure of a peroxido Mn^{III} complex bearing a non-heme ligand shows that the peroxide ligand is bound to a manganese ion symmetrically in a side-on η^2 fashion. The complex is capable of deformylating aldehydes by a nucleophilic reaction but not capable of oxygenating substrates by an electrophilic reaction. tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

Dioxygen Activation

M. S. Seo, J. Y. Kim, J. Annaraj, Y. Kim,
Y.-M. Lee, S.-J. Kim, J. Kim,*
W. Nam* ———— **377 – 380**

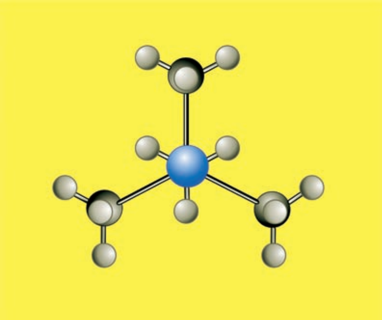
$[Mn(tmc)(O_2)]^+$: A Side-On Peroxido Manganese(III) Complex Bearing a Non-Heme Ligand

Contents

Group 14 Derivatives

J. Z. Dávalos, R. Herrero, J.-L. M. Abboud,*
O. Mó, M. Yáñez* ———— 381 – 385

How Can a Carbon Atom Be Covalently Bound to Five Ligands? The Case of $Si_2(CH_3)_7^+$

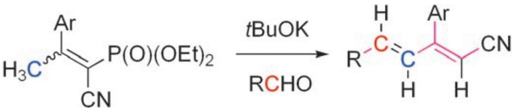


The beauty of symmetry: The $Si_2(CH_3)_7^+$ ion can be observed under the low pressures used in Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The optimized geometry of the ion, as determined from theoretical calculations and FT-ICR experimental results, reveals a C_{3h}-symmetric structure, in which a planar CH_3 group is symmetrically bonded to two eclipsed $Si(CH_3)_3$ moieties (see picture; Si blue, C dark gray, H pale gray).

Olefination Reactions

S. M. Date, S. K. Ghosh* ———— 386 – 388

A Highly Regio- and Stereoselective Vinylogous Horner–Wadsworth–Emmons Route to Densely Substituted 1,3-Butadienes

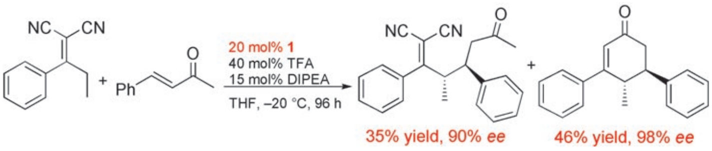


A new dimension has been given to the Horner–Wadsworth–Emmons reaction almost 50 years after its inception. In an unprecedented vinylogous version of the reaction, aldehydes and cyano-substituted vinyl phosphonates serve as substrates (see scheme). The novel transformations to form 1,3-dienes with a trisubstituted double bond exhibit very high regio- and stereoselectivities.

Asymmetric Synthesis

J.-W. Xie, W. Chen, R. Li, M. Zeng, W. Du, L. Yue, Y.-C. Chen,* Y. Wu, J. Zhu, J.-G. Deng* ———— 389 – 392

Highly Asymmetric Michael Addition to α,β-Unsaturated Ketones Catalyzed by 9-Amino-9-deoxyepiquinine

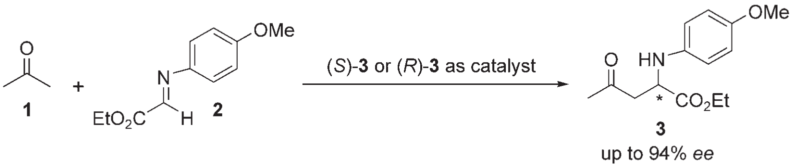


Michael–Michael–retro-Michael cascade reactions are promoted by the highly efficient organocatalyst 9-amino-9-deoxyepiquinine (**1**). The asymmetric direct vinylogous Michael addition of α,α-dicyanoalkenes to α,β-unsaturated ketones may be followed by an intramolecular Michael addition and a retro-Michael reaction to afford polysubstituted 2-cyclohexen-1-one derivatives with high enantioselectivity (see example).

Asymmetric Autocatalysis

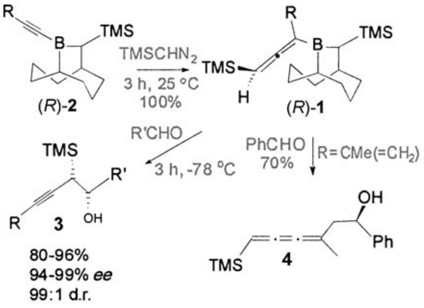
M. Mauksch,* S. B. Tsogoeva,*
I. M. Martynova, S. Wei ———— 393 – 396

Evidence of Asymmetric Autocatalysis in Organocatalytic Reactions



When product and catalyst are the same: The chiral product **3** of an asymmetric Mannich reaction (see scheme), investigated under various experimental conditions and by calculations, is shown to act as a chiral catalyst for its own formation (autocatalysis). A generally applicable catalytic cycle is proposed to involve equilibria between hydrogen-bonded substrate–product complexes.

Razzle-dazzle... and allenyl boranes **1** are obtained in enantiomerically pure form from **2** through a novel CHTMS insertion followed by a sterically driven suprafacial 1,3-borotropic rearrangement. Asymmetric allenylboration with **1** gives *syn* β-trimethylsilyl (TMS) homopropargylic alcohols **3** in 80–96% yield with d.r. 99:1 and 94–99% *ee*. When R = isopropenyl, allylboration occurs to provide the 1,2,3-trienyl alcohol **4** with > 99% *ee*.



Organoborane Chemistry

E. Canales, A. Z. Gonzalez,
J. A. Soderquist* ——— 397 – 399

Asymmetric Synthesis of Isomerically Pure Allenyl Boranes from Alkynyl Boranes through a 1,2-Insertion–1,3-Borotropic Rearrangement

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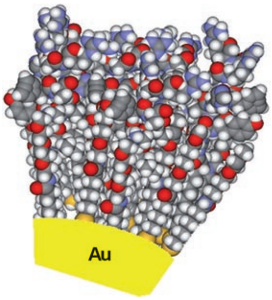
Nanozymes with a heart of gold: A functional artificial protein has been prepared by grafting a dodecapeptide onto the surface of gold nanoparticles (see picture). The system catalyzes the hydrolysis of carboxylate esters and features enzyme-like properties.



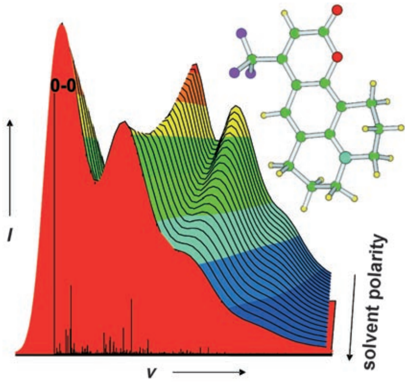
Artificial Proteins

P. Pengo, L. Baltzer, L. Pasquato,*
P. Scrimin* ——— 400 – 404

Substrate Modulation of the Activity of an Artificial Nanoesterase Made of Peptide-Functionalized Gold Nanoparticles

---

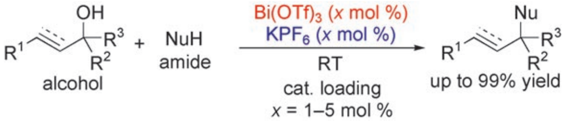
Shapes changed by solvent: An ab initio method for calculating the absorption spectra of large molecules including solvent effects and molecular vibrations shows how the solvent can shift the spectra and modulate their shapes (see picture; black lines: stick representation of absorption spectrum). The computed spectra of coumarin C153 in various solvents agree with the experimental ones.



Computer Chemistry

R. Improta,* V. Barone,*
F. Santoro* ——— 405 – 408

Ab Initio Calculations of Absorption Spectra of Large Molecules in Solution: Coumarin C153



No preactivation of the alcohol substrates is required in allylic, propargylic, and benzylic aminations catalyzed by a combination of commercially available Bi$(OTf)_3$ and KPF_6, mostly at room temperature (see scheme). The substitution reactions of readily accessible allylic, propargylic, and benzylic alcohols with sulfonamides, carbamates, and carboxamides give the desired amine products in up to 99% yield.

Amination Reactions

H. Qin, N. Yamagiwa, S. Matsunaga,*
M. Shibasaki* ——— 409 – 413

Bismuth-Catalyzed Direct Substitution of the Hydroxy Group in Alcohols with Sulfonamides, Carbamates, and Carboxamides

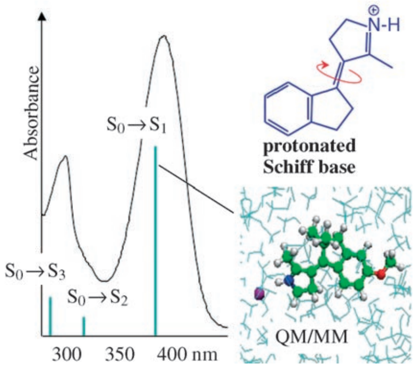
Contents

Molecular Switches

F. Lumento, V. Zanirato,* S. Fusi, E. Busi, L. Latterini, F. Elisei, A. Sinicropi, T. Andruniów, N. Ferré, R. Basosi, M. Olivucci* ______ **414–420**

Quantum Chemical Modeling and Preparation of a Biomimetic Photochemical Switch

Designing and testing biomimetic switches: Multireference perturbation theory is used to model a light-driven molecular switch featuring the same photoisomerization mechanism as the chromophore of the visual pigment rhodopsin (see picture; QM/MM: quantum mechanics/molecular mechanics). By exploiting a synthetic route based on nitrilium-cation cyclization, it was shown that the designed system can indeed be prepared and characterized.

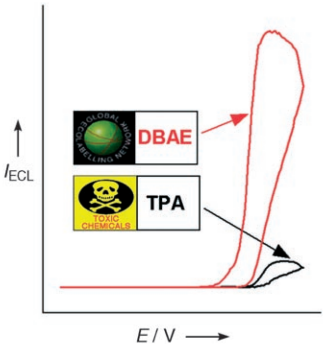


Electrochemiluminescence

X. Q. Liu, L. H. Shi, W. X. Niu, H. J. Li, G. B. Xu* ______ **421–424**

Environmentally Friendly and Highly Sensitive Ruthenium(II) Tris(2,2′-bipyridyl) Electrochemiluminescent System Using 2-(Dibutylamino)ethanol as Co-Reactant

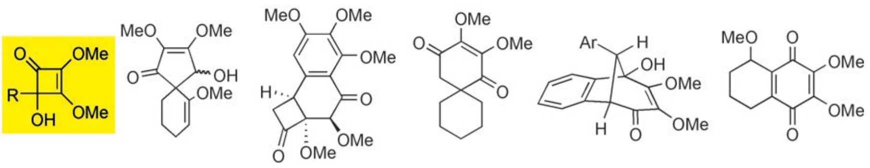
Electric light orchestra: The electrochemiluminescence (ECL) intensity of the $[Ru(bpy)_3]^{2+}$/2-(dibutylamino)ethanol (DBAE) system at Au and Pt electrodes are about 10 and 100 times, respectively, greater than that of the commonly used $[Ru(bpy)_3]^{2+}$/tripropylamine (TPA) system (see picture). Thus, DBAE is a promising co-reactant for $[Ru(bpy)_3]^{2+}$ ECL immunoassays and DNA probe assays.



Rearrangement

D. C. Harrowven,* D. D. Pascoe, I. L. Guy ______ **425–428**

Thermally Induced Cyclobutenone Rearrangements and Domino Reactions

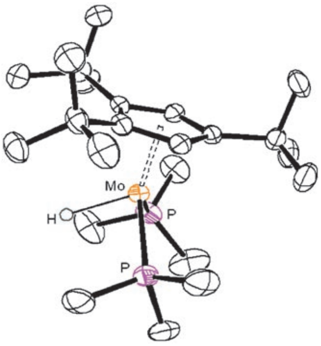


Four thermal-rearrangement pathways and a domino reaction leading to quinones arise from the thermolysis of cyclobutenones. The course of vinylcyclobutenone rearrangements is dictated by the nature of the substituent, R (see scheme): a cyclopentenone arises when R is an electron-rich alkene. In other cases thermolysis gives a cyclohexadienone, which may collapse with elimination to form a quinone, or tautomerize into a hydroquinone or cyclohexenedione.

Paramagnetic Hydride Complexes

M. Baya, J. Houghton, J.-C. Daran, R. Poli* ______ **429–432**

Formation and Structure of a Sterically Protected Molybdenum Hydride Complex with a 15-Electron Configuration: $[(1,2,4\text{-}C_5H_2tBu_3)Mo(PMe_3)_2H]^+$

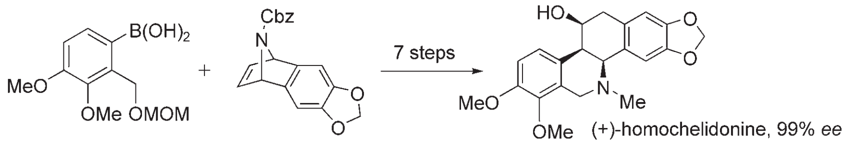


Got to get up to get down: Oxidation of $[(1,2,4\text{-}C_5H_2tBu_3)Mo(PMe_3)_2H_3]$ induces H_2 reductive elimination and yields the first stable 15-electron molybdenum hydride complex, $[(1,2,4\text{-}C_5H_2tBu_3)Mo(PMe_3)_2H]^+$ (see picture). The stability of this complex can be attributed to steric protection, as no additional electron density is available on the ligands for a π-stabilization mechanism.

Natural Products Synthesis

H. A. McManus, M. J. Fleming,
M. Lautens* ——— **433 – 436**

Enantioselective Total Synthesis of (+)-Homochelidonine by a Pd^{II}-Catalyzed Asymmetric Ring-Opening Reaction of a *meso*-Azabicyclic Alkene with an Aryl Boronic Acid

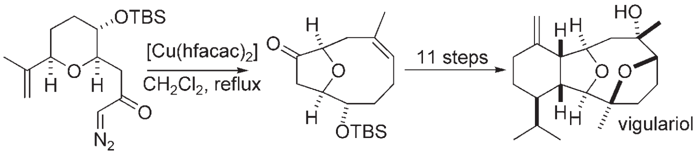


An efficient and highly convergent enantioselective synthesis of (+)-homochelidonine has been achieved (see scheme; Cbz = benzyloxycarbonyl, MOM = methoxymethyl) and relied on a new and powerful desymmetrizing ring-opening reaction of a *meso*-azabicycle with an aryl boronic acid. The route should allow access to other hexahydrobenzo[*c*]phenanthridine alkaloids.

Natural Product Synthesis

J. S. Clark,* S. T. Hayes, C. Wilson,
L. Gobbi ——— **437 – 440**

A Concise Total Synthesis of (±)-Vigulariol

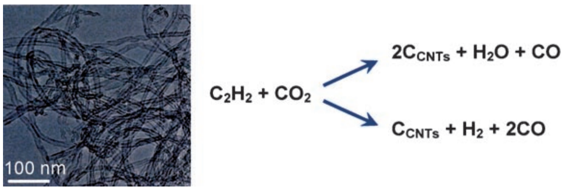


From the deep: Vigulariol has been efficiently synthesized in 20 steps and 4.0% overall yield from commercially available starting materials. Key to the synthesis was the use of copper(II) hexafluoroacetylacetate [Cu(hfacac)$_2$] to form the oxabicyclo[6.2.1]undecene system (see scheme; TBS = *tert*-butyldimethylsilyl). The strategy should provide access to other members of the cladiellin family.

Nanotubes

A. Magrez,* J. W. Seo, V. L. Kuznetsov,
L. Forró ——— **441 – 444**

Evidence of an Equimolar C_2H_2–CO_2 Reaction in the Synthesis of Carbon Nanotubes

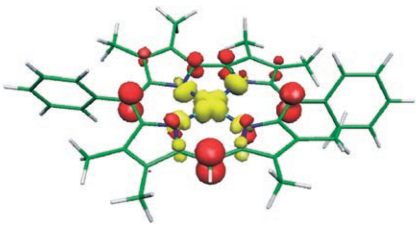


Meeting point: Carbon nanotubes (CNTs) are produced by an equimolar reaction between C_2H_2 and CO_2 (see scheme). CO_2 can be introduced as a gas or a carbonate support of the metal particles. When $CaCO_3$ is used, the growth of a nanotube stems from the triple-point junction, which corresponds to the area surrounding the metal support interface where CO_2, C_2H_2, and the support meet.

Electronic Structure

M. Bröring,* F. Brégier, E. Cónsul Tejero,
C. Hell, M. C. Holthausen* ——— **445 – 448**

Revisiting the Electronic Ground State of Copper Corroles

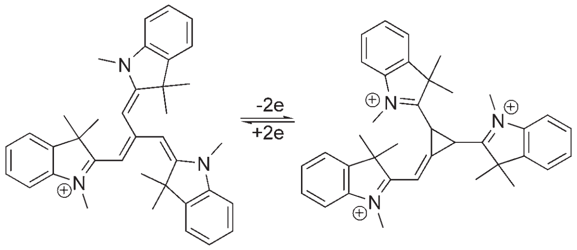


Back in the saddle: Copper corroles do not contain a Cu^{III} ion, but rather a well-hidden Cu^{II} ion. A comparative crystallographic and theoretical study (see spin-density representation) of isostructural corroloid complexes with copper ions in different formal oxidation states suggests that the divalent state is stabilized through a saddling distortion of the corrole ligand.

Cyanine Dyes

H. John, C. Briehn, J. Schmidt, S. Hünig,*
J. Heinze* ______________ **449–453**

Trinuclear Cyanines (TNCs) Revisited: A New Class of Electrochromics by Intramolecular π/σ Switching

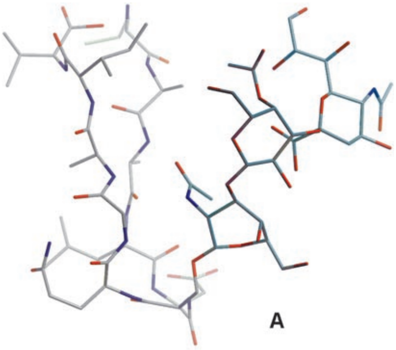


The Y-shaped π systems in trinuclear cyanines can, through a formal two-electron transfer, form a core methylenecyclopropane unit with three shorter, isolated π systems (see picture). Studies of the spectroelectrochemistry verify the reversibility of this redox reaction, which has an unusually pronounced electrochromism.

Glycopeptides

A. Kuhn, H. Kunz* ______________ **454–458**

Saccharide-Induced Peptide Conformation in Glycopeptides of the Recognition Region of LI-Cadherin



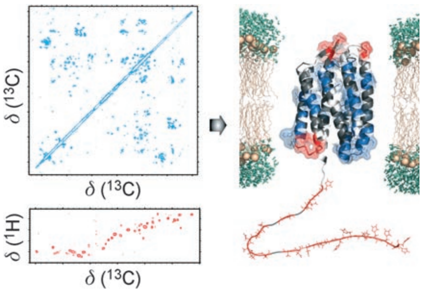
The type and the size of the saccharide side chain can affect the conformation of the peptide portion of glycopeptides. This was shown by conformational analysis in solution for a series of glycoundecapeptides with systematically varied tumor-associated carbohydrate antigens of type **A** from the recognition region of the cell adhesion glycoprotein LI-cadherin (gray C, red O, blue N; the saccharide side chain is more intensely colored).

Solid-State NMR Spectroscopy

M. Etzkorn, S. Martell, O. C. Andronesi,
K. Seidel, M. Engelhard,*
M. Baldus* ______________ **459–462**

Secondary Structure, Dynamics, and Topology of a Seven-Helix Receptor in Native Membranes, Studied by Solid-State NMR Spectroscopy

In the loop: High-resolution solid-state NMR spectroscopy is used to study the secondary structure, dynamics, and membrane topology of an entire seven-helix receptor, sensory rhodopsin II from *Natronomonas pharaonis* (see picture). The experiments are carried out on a single isotope-labeled sample in a native membrane environment.

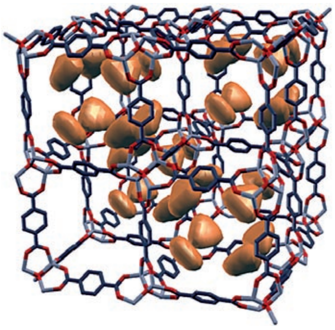


VIP

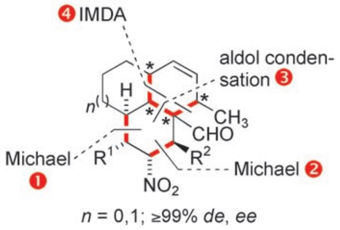
Diffusion in Solids

S. Amirjalayer, M. Tafipolsky,
R. Schmid* ______________ **463–466**

Molecular Dynamics Simulation of Benzene Diffusion in MOF-5: Importance of Lattice Dynamics



Doing the locomotion: When benzene molecules diffuse through the metal organic framework MOF-5, they accumulate in pockets (see picture). Molecular dynamics simulations reveal that the correlated lattice motion increases this binding. Only when the the lattice dynamics are considered in the simulation, can the experimental diffusion constants be reproduced.



Hitting the teens! Five C–C bonds and eight stereocenters were formed in a one-pot asymmetric multicomponent domino reaction, which led to the functionalized tricyclic diterpenoid-type core structures (see scheme, IMDA = intramolecular Diels–Alder reaction).

Polycycles

D. Enders,* M. R. M. Hüttl, J. Runsink, G. Raabe, B. Wendt ——— **467 – 469**

Organocatalytic One-Pot Asymmetric Synthesis of Functionalized Tricyclic Carbon Frameworks from a Triple-Cascade/Diels–Alder Sequence

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

A video clip is available as Supporting Information on the WWW (see article for access details).

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Service