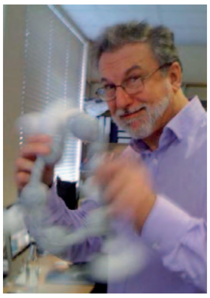
The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

Author Profile

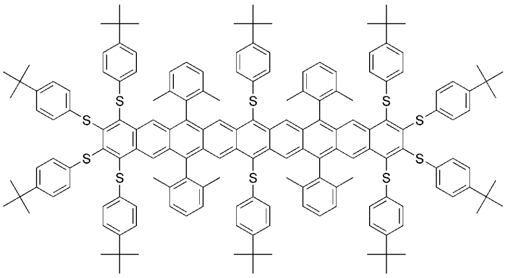


"When I wake up I drink coffee. If I could be anyone for a day, I would be Lewis Carroll. He worked just down the road from here. But, only for a day.
The most significant scientific advance of the last 100 years has been the human genome sequence through a wonderful amalgamation of biology, chemistry, engineering, computer hardware and software, and management skills. Plus some adroit politics …"
This and more about Hagan Bayley can be found on page 4010.

Books

Highlights

Larger Acenes



The bigger, the better: In the last decade, the development of organic electronics, and particularly of organic field-effect transistors, carbon nanotubes, and graphene, has spurred efforts to prepare larger acenes. Stable, large acenes have been obtained and fully characterized. Developments in the synthesis of heptacenes, as well as the very recent synthesis of octacene and nonacenes, are highlighted.

Essays

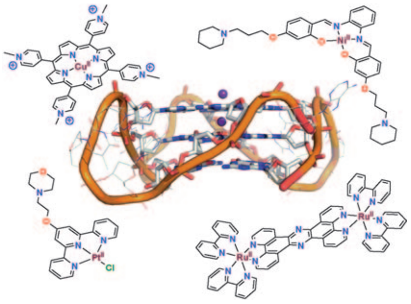
Chemistry of Life

David versus Goliath: Since the first synthesis of urea by F. Wöhler (see portrait) in 1828, chemistry has played a major role in the decline of vitalism through its reductionist approaches and has continuously provided remarkable contributions to the understanding of the nature of life. Future progress in the emerging postgenomic era resides in the balanced combination of chemistry and integrative biology.

Reviews

Bioinorganic Chemistry

Guanine-rich sequences of nucleic acids can assemble into tetrastranded structures. The resulting G-quadruplexes have been identified as potential targets for the development of anticancer drugs and have sparked great interest in the design of molecules that can stabilize quadruplex structures. This Review presents an overview of the interaction of metal complexes with G-quadruplex DNA, highlights their potential use as anticancer drugs and as molecular probes.



Communications

Ring-Expansion Reactions

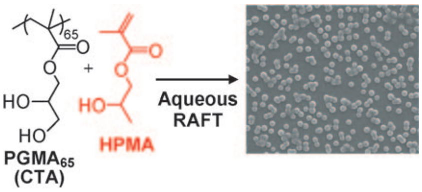
A cut and shut job: The highly selective title reaction proceeds, using O_2 as the oxidant, to afford tetrahydroquinoline derivatives. This chemistry offers a new approach to polysubstituted 4,5-dihydrocyclopenta[*c*]quinolines, and also valuable mechanistic insight into this ring-expansion reaction.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 9442/8583 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Aqueous RAFT Synthesis

Y. Li, S. P. Armes* ________ 4042–4046

RAFT Synthesis of Sterically Stabilized Methacrylic Nanolatexes and Vesicles by Aqueous Dispersion Polymerization

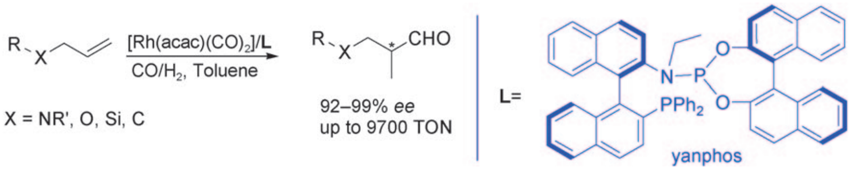


Size control: Sterically stabilized methacrylic nanolatexes are readily prepared by aqueous dispersion polymerization using RAFT reactions (see scheme; CTA = chain transfer agent). Varying the length of the poly(HPMA) chains allows precise size control of the nanolatex particles.

Asymmetric Hydroformylation

X. Zhang, B. Cao, S. Yu,
X. Zhang* ________ 4047–4050

Rhodium-Catalyzed Asymmetric Hydroformylation of *N*-Allylamides: Highly Enantioselective Approach to β^2-Amino Aldehydes

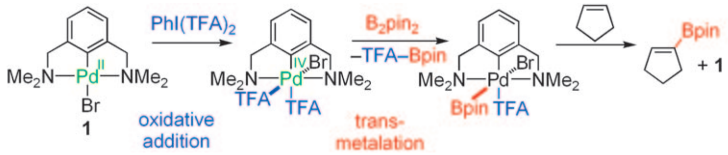


You're having a lahf! The asymmetric hydroformylation (AHF) of allylic compounds, catalyzed by a rhodium–yanphos complex, is a direct and concise route to β^2-amino aldehydes, acids, and alcohols with excellent enantioselectivity (see scheme; TON = turnover number, acac = acetylacetonate).

Alkene Borylation

N. Selander, B. Willy,
K. J. Szabó* ________ 4051–4053

Selective C–H Borylation of Alkenes by Palladium Pincer Complex Catalyzed Oxidative Functionalization

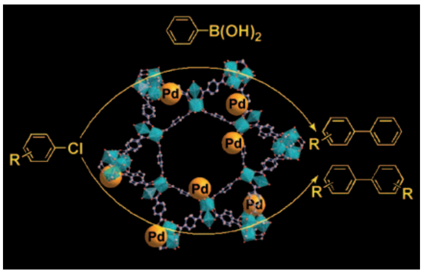


The C–H borylation of simple alkenes catalyzed by palladium pincer complex **1** was performed in the presence of hypervalent iodine and bis(pinacolato)diboron compounds. The borylation reaction probably occurs by a $\mathrm{Pd^{II}} \rightarrow \mathrm{Pd^{IV}}$ oxidation–diboronate transmetalation sequence. TFA = trifluoroacetate.

Coupling Reactions

B. Z. Yuan, Y. Y. Pan, Y. W. Li,* B. L. Yin,
H. F. Jiang* ________ 4054–4058

A Highly Active Heterogeneous Palladium Catalyst for the Suzuki–Miyaura and Ullmann Coupling Reactions of Aryl Chlorides in Aqueous Media



A heterogeneous palladium catalyst, which is supported on a metal–organic framework, MIL-101, is highly efficient in water-mediated coupling reactions of chloroarenes. High yields are obtained in Suzuki–Miyaura cross-coupling and Ullmann homocoupling reactions of substituted aryl chlorides. Furthermore, the catalyst is easily recoverable and reusable (see picture; Cr blue, O red, C white).

For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 9442/8583 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

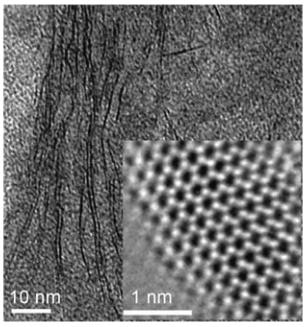
Contents

Layered Compounds

H. S. S. Ramakrishna Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati, C. N. R. Rao* ——— **4059 – 4062**

MoS_2 and WS_2 Analogues of Graphene

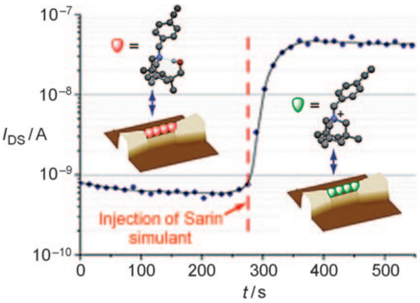
Inorganic sheets: Graphene-like MoS_2 and WS_2 were prepared by three different chemical methods. Examination by microscopic techniques revealed that they consist of one or a few layers (see depicted TEM image of WS_2 layers), and an atomic-resolution TEM image showed that layered MoS_2 has a hexagonal arrangement of Mo and S atoms (see inset).



Nerve Agent Sensors

S. Clavaguera, A. Carella,* L. Caillier, C. Celle, J. Pécaut, S. Lenfant, D. Vuillaume, J.-P. Simonato* ——— **4063 – 4066**

Sub-ppm Detection of Nerve Agents Using Chemically Functionalized Silicon Nanoribbon Field-Effect Transistors

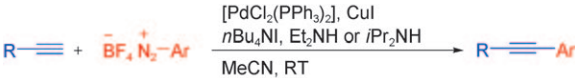


A chemical receptor specific to traces of organophosphorus agents (OPs) has been synthesized and grafted to a silicon nanoribbon field-effect transistor (SiNR-FET). X-ray structures illustrate the structural modifications of the receptor upon exposure to nerve agent simulants. A highly sensitive and selective detector of OPs can be obtained by monitoring the Drain-Source current of the SiNR-FET at an optimum back-gate voltage as a function of time.

Cross-Coupling

G. Fabrizi, A. Goggiamani, A. Sferrazza, S. Cacchi* ——— **4067 – 4070**

Sonogashira Cross-Coupling of Arenediazonium Salts

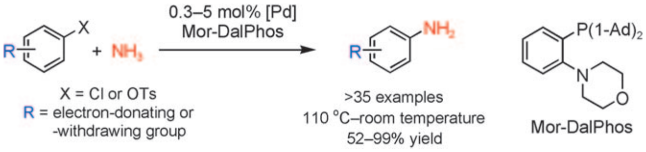


Star-crossed lovers: The domino iododediazoniation/Sonogashira cross-coupling of terminal alkynes with arenediazonium salts has been developed. The arenediazonium salt synthesis/iododediazoniation/Sonogashira cross-coupling sequence can also be performed as a one-pot process, omitting the isolation of the arenediazonium salt.

Ammonia Arylation

R. J. Lundgren, B. D. Peters, P. G. Alsabeh, M. Stradiotto* ——— **4071 – 4074**

A P,N-Ligand for Palladium-Catalyzed Ammonia Arylation: Coupling of Deactivated Aryl Chlorides, Chemoselective Arylations, and Room Temperature Reactions

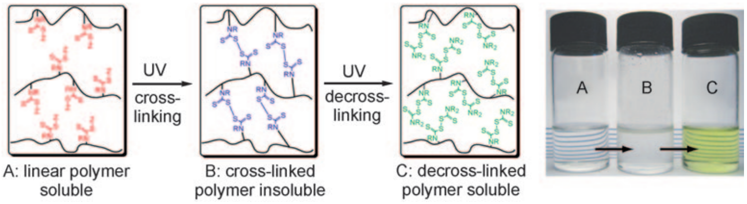


Amazing ammonia: A new air-stable P,N-ligand (Mor-DalPhos) is reported that enables the palladium-catalyzed cross-coupling of ammonia to a variety of aryl chloride and aryl tosylate substrates with high chemoselectivity and, for the first time, at room temperature (see scheme; Ad = adamantyl, Ts = *para*-toluenesulfonyl).

Polymer Cross-Linking/De-Linking

L. M. García-Con, M. J. Whitcombe,*
E. V. Piletska, S. A. Piletsky **4075 – 4078**

A Sulfur–Sulfur Cross-Linked Polymer Synthesized from a Polymerizable Dithiocarbamate as a Source of Dormant Radicals

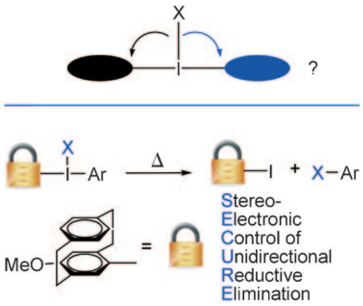


Cross on UV light: A polymer bearing dithiocarbamate ester groups, linked to the polymer backbone through the dithiocarbamate nitrogen atom is capable of reversible cross-linking and de-linking through photochemical rearrangement of the pendant groups (see scheme).

Stereoelectronic Control

B. Wang, J. W. Graskemper, L. Qin,
S. G. DiMagno* **4079 – 4083**

Regiospecific Reductive Elimination from Diaryliodonium Salts

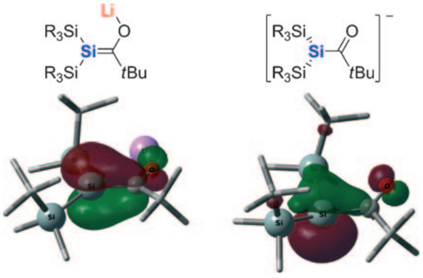


Out-of-plane steric bulk furnished by a cyclophane substituent on iodine(III) strongly destabilizes the transition state in the reductive elimination from diaryliodonium salts and leads to regiochemical control (dubbed SECURE), as is demonstrated by computational and experimental studies. This approach should be general for high-valent main-group and transition metal ions. X = N_3, OAc, PhO, CF_3CH_2O, SCN, PhS.

Silicon Enolate Analogues

R. Dobrovetsky, L. Zborovsky, D. Sheberla,
M. Botoshansky, D. Bravo-Zhivotovskii,*
Y. Apeloig* **4084 – 4087**

Isolation of Silenolates $(R_3Si)_2Si{=}C(OLi)Ad$ with a Doubly Bonded Silicon Atom

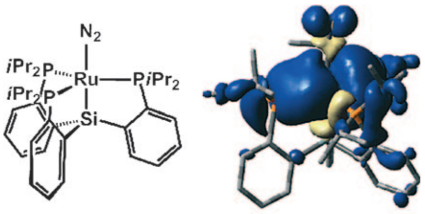


The first enol silenolates, $(tBuMe_2Si)_2Si{=}C(OLi)Ad$ and $(tBu_2MeSi)_2Si{=}C(OLi)Ad$, were synthesized and characterized by X-ray spectroscopy. Calculations show that, in contrast to organic enolates, which exist predominantly in the enol form regardless of solvation, the enol form of silenolates (left) is favored in nonpolar solvents, and the keto form (right) when strongly solvated. Ad = 1-adamantyl.

Metalloradical Complexes

A. Takaoka, L. C. H. Gerber,
J. C. Peters* **4088 – 4091**

Access to Well-Defined Ruthenium(I) and Osmium(I) Metalloradicals

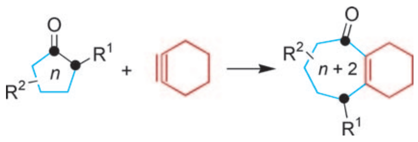


Radically complex: Well-defined mononuclear Ru^I and Os^I complexes (see scheme) have metalloradical character, as indicated by EPR spectroscopy and DFT calculations. The Ru^I and Os^I metalloradicals exhibit both one-electron and two-electron redox reactivity. The latter process affords unusual imido complexes with substantial radical character on the {ArN} moiety.

Ring-Expansion Reactions

C. M. Gampe, S. Boulos,
E. M. Carreira* **4092 – 4095**

Cyclohexyne Cycloinsertion by an Annulative Ring Expansion Cascade



Cyclohexyne steps into the ring! Cyclohexyne is used for the facile synthesis of polycyclic, medium sized rings. Its insertion into cyclic ketones enables rapid access to densely functionalized building blocks.

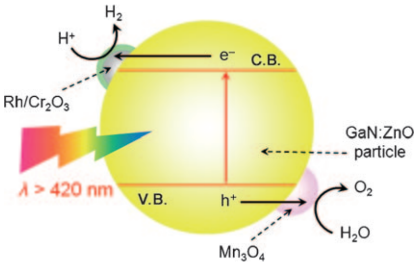
Contents

Photocatalysis

K. Maeda, A. Xiong, T. Yoshinaga, T. Ikeda, N. Sakamoto, T. Hisatomi, M. Takashima, D. Lu, M. Kanehara, T. Setoyama, T. Teranishi, K. Domen* ____ 4096 – 4099

Photocatalytic Overall Water Splitting Promoted by Two Different Cocatalysts for Hydrogen and Oxygen Evolution under Visible Light

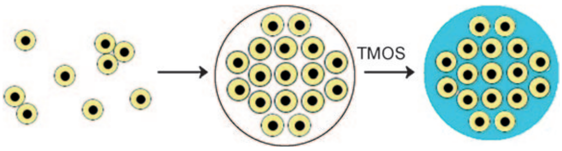
In harmony: Nanoparticles of Mn_3O_4 and core/shell-structured Rh/Cr_2O_3 as cocatalysts on the surface of a solid solution of GaN and ZnO as catalyst promote O_2 and H_2 evolution, respectively, under visible light ($\lambda > 420$ nm), thereby achieving enhanced water-splitting activity compared to analogues modified with either Mn_3O_4 or Rh/Cr_2O_3.



Protein Crystals

E. M. Lambert, C. Viravaidya, M. Li, S. Mann* ____ 4100 – 4103

Microemulsion-Mediated Self-Assembly and Silicification of Mesostructured Ferritin Nanocrystals

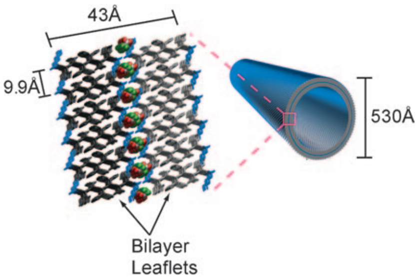


Protein crystals turned to stone: Protein-mediated aggregation of microemulsion water droplets is used to prepare discrete ferritin nanocrystals with periodically arranged close packed structures. Addition of tetramethoxysilane (TMOS) to the microemulsion produces silica-ferritin hybrid nanoparticles with well-ordered mesostructured interiors (see scheme).

Self-Assembly

W. S. Childers, A. K. Mehta, R. Ni, J. V. Taylor, D. G. Lynn* ____ 4104 – 4107

Peptides Organized as Bilayer Membranes

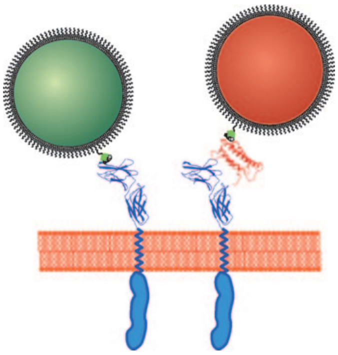


A buried polar bilayer interface composed of interdigitated peptide ends and a high density of CF_3COO^- counterions passifying lysine amines are identified in nanotubes obtained by self-assembly of short peptides. The structure reveals distinct characteristics that differentiate peptide bilayers and lipid bilayers that can now be exploited for the construction of lipid-like nanomaterials with protein functionality.

Nanoparticle Functionalization

C. You, S. Wilmes, O. Beutel, S. Löchte, Y. Podoplelowa, F. Roder, C. Richter, T. Seine, D. Schaible, G. Uzé, S. Clarke, F. Pinaud, M. Dahan, J. Piehler* ____ 4108 – 4112

Self-Controlled Monofunctionalization of Quantum Dots for Multiplexed Protein Tracking in Live Cells

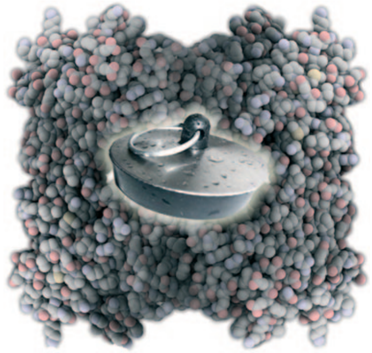


Functionalization of quantum dots (QDs) was achieved by controlling the surface density of functional groups by electrostatic repulsion. These QDs were conjugated with His-tagged proteins in vitro and in live cells by self-assembly without requiring further fractionation, and dual-color tracking of cell surface receptors was possible.

Enzyme Inhibition

P. R. Wich, C. Schmuck* —— **4113–4116**

Reversible and Noncompetitive Inhibition of β-Tryptase by Protein Surface Binding of Tetravalent Peptide Ligands Identified from a Combinatorial Split–Mix Library

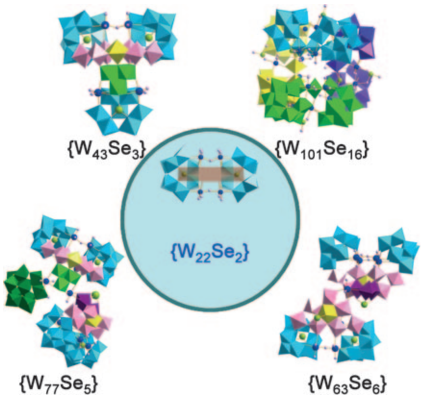


Molecular plug: On-bead screening of a combinatorial library of 216 tetravalent oligopeptides reveals highly specific, noncompetitive inhibitors of the serine protease β-tryptase with nanomolar affinity. The ligands most likely bind to the protein surface and act as a molecular plug that blocks access to the active sites, which are buried inside a central cavity (see picture).

Polyoxometalates

J. Yan, D.-L. Long,*
L. Cronin* ———— **4117–4120**

Development of a Building Block Strategy To Access Gigantic Nanoscale Heteropolyoxotungstates by Using SeO_3^{2-} as a Template Linker

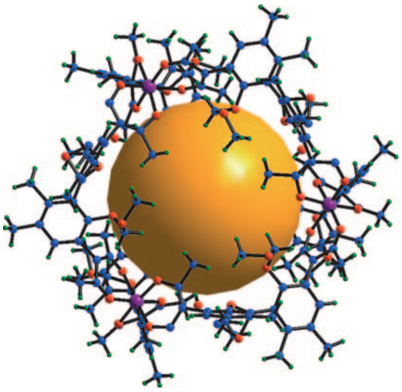


Heteroatom control in the assembly of nanoscale gigantic heteropolyoxotungstates was accomplished by using SeO_3^{2-} to give $[H_2W_{43}Se_3O_{148}]^{24-}$ $\{W_{43}Se_3\}$, $[H_4W_{77}Se_5O_{265}]^{44-}$ $\{W_{77}Se_5\}$, $[H_6W_{63}Se_6O_{221}]^{34-}$ $\{W_{63}Se_6\}$, and $[H_8W_{100}Se_{16}O_{364}]^{56-}$ $\{W_{101}Se_{16}\}$ cluster anions. The clusters are all derived from a common $\{W_{22}Se_2\}$ building block and are constructed without the need to employ addition heterometallic linkers; the three smaller clusters incorporate pentagonal $W(W_4)$ units.

Host–Guest Systems

T. Liu, Y. Liu, W. Xuan,
Y. Cui* ———— **4121–4124**

Chiral Nanoscale Metal–Organic Tetrahedral Cages: Diastereoselective Self-Assembly and Enantioselective Separation

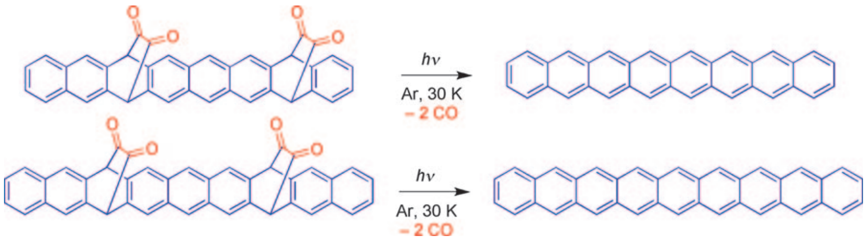


Cage rage: Chiral tetrahedral cages are diastereoselectively self-assembled from enantiopure C_2-symmetric biphenyl bis(β-diketonate) linkers and C_3-symmetric octahedral Fe^{3+} or Ga^{3+} ions (see picture; Fe purple, C blue, O red; cavity shown as an orange sphere). The porous polyhedra exhibit metal-dependent chiroptical behavior and act as hosts for the crystallization separation of racemic alcohols with up to 99.5% *ee*.

Acene Homologues

C. Tönshoff,
H. F. Bettinger* ———— **4125–4128**

Photogeneration of Octacene and Nonacene



Take it to the limit: Parent acenes larger than heptacene have eluded synthesis for decades. When 1,2-diketone bridges in suitably designed tetraketone precursors were removed by irradiation under matrix-isolation conditions (see scheme), the parent systems of the two next higher acenes were accessible experimentally.

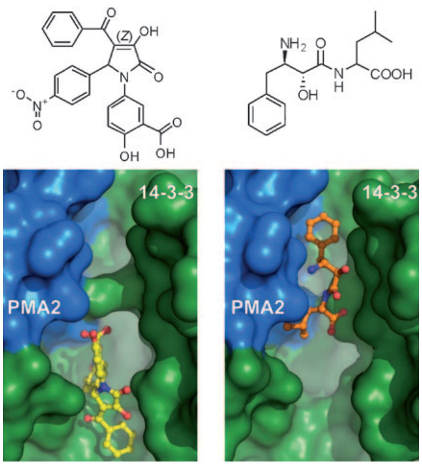
Contents

Protein–Protein Interactions

R. Rose, S. Erdmann, S. Bovens, A. Wolf,
M. Rose, S. Hennig, H. Waldmann,
C. Ottmann* ____ **4129–4132**

Identification and Structure of Small-Molecule Stabilizers of 14–3–3 Protein–Protein Interactions

Two structurally unrelated small molecules that stabilize the interaction of a 14–3–3 protein with the proton pump PMA2 have been identified. The compounds are selective among different 14–3–3 protein–protein interactions and are active in vivo. Crystal structures of ternary complexes revealed that the molecules bind to different sites in the interface of the 14–3–3 protein and PMA2 (see picture), thus explaining the different binding kinetics.

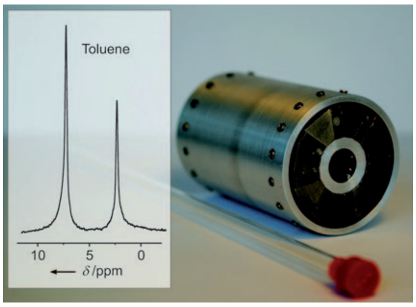


NMR Techniques

E. Danieli, J. Perlo, B. Blümich,
F. Casanova* ____ **4133–4135**

Small Magnets for Portable NMR Spectrometers

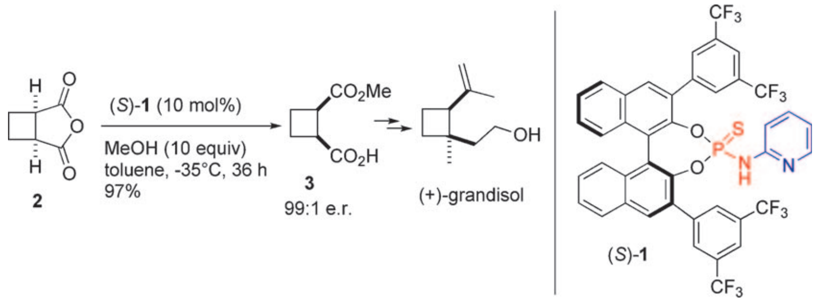
Downsizing: A pocket-size permanent magnet has been constructed that is suitable for measuring ^{1}H NMR spectra of samples in standard NMR tubes. The new shimming approach implemented to overcome the inherent inhomogeneity of permanent magnets opens the door to compact high-resolution NMR spectrometers for conventional samples.



Asymmetric Catalysis

V. N. Wakchaure, B. List* ____ **4136–4139**

A New Structural Motif for Bifunctional Brønsted Acid/Base Organocatalysis



Naturally synthetic: Acid/base catalyst (*S*)-**1** can be used in highly enantioselective alcoholytic desymmetrizations of *meso* anhydrides. For example, the methanolysis of cyclobutane anhydride derivative **2** gave hemiester **3** in 99:1 e.r. (see scheme). Ester **3** was used in a short enantioselective synthesis of (+)-grandisol.

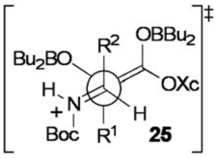
Supporting information is available on www.angewandte.org (see article for access details).

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

Service

Corrigendum

The structure for transition state **25** in Scheme 1 of this Communication (DOI: 10.1002/anie.201000609) was drawn incorrectly. A corrected transition-state structure consistent with the stereochemical outcome in the formation of **16**–**18** is depicted below.
In addition, incorrect quantities of dibutylboron triflate and triethylamine were provided in the experimental section. The correct quantities are: 1 M solution of dibutylboron triflate in dichloromethane (450 µL, 0.45 mmol); triethylamine (78 µL, 0.56 mmol).



25

Asymmetric Tandem Wittig Rearrangement/Mannich Reactions

N. C. Giampietro
J. P. Wolfe* 2922–2924

Angew. Chem. Int. Ed. **2010**, *49*

DOI 10.1002/anie.201000609