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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:

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Fluorous-Based Small-Molecule Microarrays for the Discovery of Histone Deacetylase Inhibitors

*H. Chen, S. Yang, A. Wortmann, R. Zenobi**
Neutral Desorption Sampling of Living Objects for Rapid Analyses by Extractive Electrospray Ionization Mass Spectrometry

M. Diefenbach, K. Kim**
Towards Molecular Magnetic Switching with an Electric Bias

*W. Monillas, G. A. Yap, K. Theopold**
A Tale of Two Isomers: A Stable Phenyl Hydride and a High-Spin (S=3) Benzene Complex of Chromium

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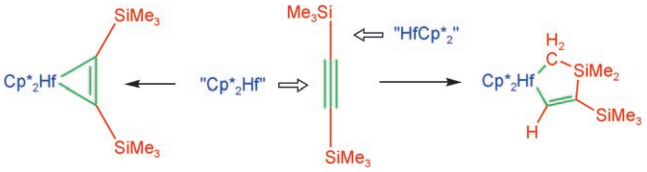
A. Ian Scott (1928–2007) — *P. Shoolingin-Jordan* ______ **6768**

Highlights

Bond Activation

C. Marschner* ______ **6770 – 6771**

Hafnium: Stepping into the Limelight!

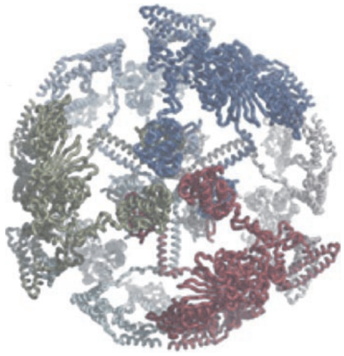


Worth the wait! Hafnium, a largely underrated element, showed unexpected C–H and Si–C bond activation chemistry, which was found during the course of the first synthesis of hafniumbis(silyl)alkyne complexes. As for the case of N_2-activation, hafnium proves to be superior to zirconium in this respect.

Molecular Machines

T. Kolter* ______ **6772 – 6775**

The Fatty Acid Factory of Yeasts



Fatty acids are essential metabolites for nearly all organisms. Yeasts, fungi, and animals synthesize them using fatty acid synthases of type I (FAS I) in the cytoplasm, whereby the FAS I of animals is distinct from that of fungi and yeasts. Recently obtained high-resolution X-ray structures of the 2.6-MDa FAS enzyme from yeast and fungi (see picture) now allow a closer look at the mechanism of this reaction.

Essays

The discovery of cell-free alcohol fermentation: In 1897 Eduard Buchner laid the foundation stone for modern in vitro enzymology from his studies on the conversion of sugar into ethanol in the presence of zymase derived from yeast. The resulting Nobel Prize in Chemistry was awarded to Buchner one hundred years ago in 1907.

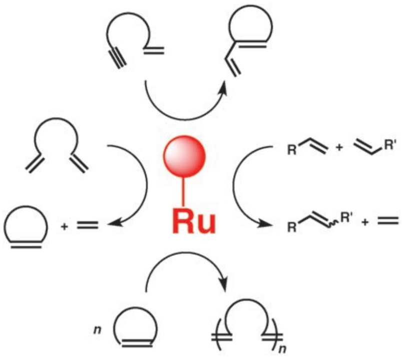
History of Science

L. Jaenicke* ______ **6776–6782**

Centenary of the Award of a Nobel Prize to Eduard Buchner, the Father of Biochemistry in a Test Tube and Thus of Experimental Molecular Bioscience

Reviews

Thinking green: One of the challenging goals of modern chemistry is the development of clean and environmentally friendly processes, particularly as the number of transition-metal-catalyzed processes is increasing. With the example of ruthenium-catalyzed olefin metathesis, a comprehensive and critical overview is provided of the recent progress achieved in this area.

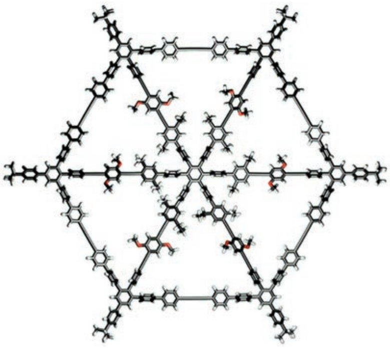


Green Metathesis Reactions

H. Clavier,* K. Grela,* A. Kirschning,* M. Mauduit,* S. P. Nolan* _ **6786–6801**

Sustainable Concepts in Olefin Metathesis

Communications



A template-directed sixfold dimerization of alkyne units is the final step in the synthesis of the title compound leading to nanoscale 2D rigid wheel-shaped oligo(phenylene ethynylene)s. Solubilizing side groups allow full characterization by NMR spectroscopy, GPC, MALDI-TOF MS, and STM. The distance between two peripheral *tert*-butyl groups at opposite sites of the oligomer is estimated to be 7 nm.

Two-Dimensional Oligomers VIP

D. Mössinger, J. Hornung, S. Lei, S. De Feyter,* S. Höger* ___ **6802–6806**

Molecularly Defined Shape-Persistent 2D Oligomers: The Covalent-Template Approach to Molecular Spoked Wheels

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2006–45/34

2nd September Issue

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Y. Lu

Carbene Carbonylation
T. T. Tidwell

Repairing DNA Damage
H.-A. Wagenknecht

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Although *Angewandte Chemie* is owned by the German Chemical Society (Gesellschaft Deutscher Chemiker, GDCh) and is published by Wiley-VCH in a charming small town in southwest Germany, it is international in every other respect. Authors and referees from around the globe contribute to its success. Most of the articles are submitted from China (20%), USA (16%), and Japan (13%) - only then comes Germany (12%). Most of the referee reports come from Germany and the USA, but Japan and Western Europe are also well represented.

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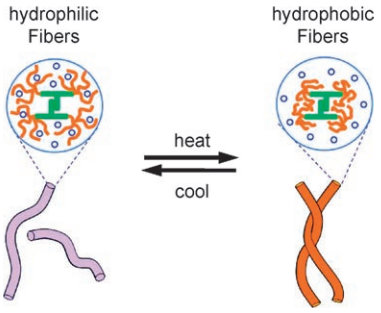

Stimulating fibers: Self-assembled nanofibers coated with hydrophilic oligo(ethylene oxide) dendrons transform reversibly, upon heating, into hydrophobic nanofiber bundles as a result of dehydration of the dendritic chains (see scheme). A thermoresponsive sol–gel phase transition is observed.

Amphiphilic Nanofibers

K.-S. Moon, H.-J. Kim, E. Lee, M. Lee* ______ **6807 – 6810**

Self-Assembly of T-Shaped Aromatic Amphiphiles into Stimulus-Responsive Nanofibers

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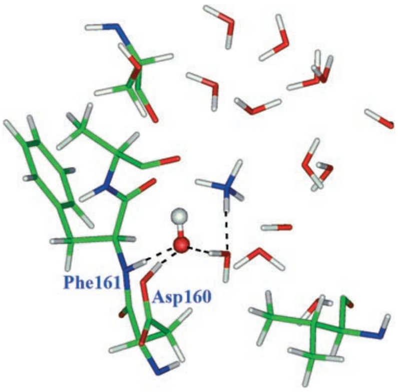

All wired up: In the ammonia-channel protein AmtB, the deprotonation of NH_4^+ can occur along a hydrogen-bond wire that contains two water molecules and terminates at the proton acceptor, the carboxylate group of the residue Asp160 (see picture). The results of quantum-mechanical and quantum-mechanical/molecular-mechanical calculations suggest that a stepwise rather than a concerted mechanism is involved.

Computational Biology

Z. Cao,* Y. Mo,* W. Thiel ______ **6811 – 6815**

Deprotonation Mechanism of NH_4^+ in the *Escherichia coli* Ammonium Transporter AmtB: Insight from QM and QM/MM Calculations

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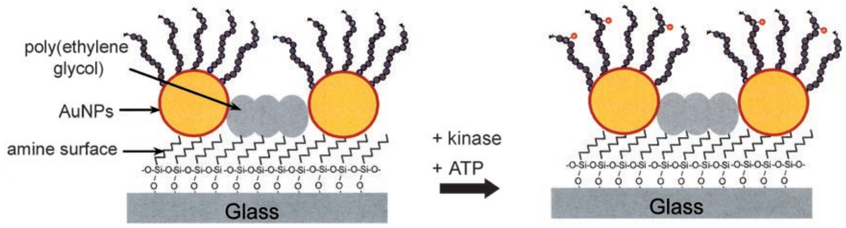

Spot the mass of peptides: A label-free protein kinase assay that uses secondary-ion mass spectrometric imaging has been demonstrated with peptide-conjugated gold nanoparticles (AuNPs). With detection of the mass change of peptide substrates in a kinase reaction, AuNP-enhanced peptide signals enabled the assaying of both the protein kinase and its inhibition by chemical imaging of peptide substrates on a surface (see picture).

Enzyme Assays

Y.-P. Kim, E. Oh, Y.-H. Oh, D. W. Moon, T. G. Lee,* H.-S. Kim* ______ **6816 – 6819**

Protein Kinase Assay on Peptide-Conjugated Gold Nanoparticles by Using Secondary-Ion Mass Spectrometric Imaging

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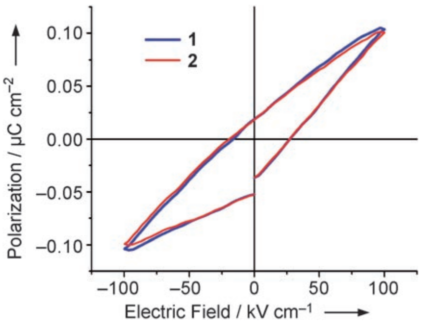


Eu-reka! Two neutral mononuclear europium enantiomers $[Eu(tta)_3L]$ and their thin films were prepared (tta = 2-thenoyltrifluoroacetonate; L = (−)-4,5-pinene bipyridine (**1**), L = (+)-4,5-pinene bipyridine (**2**)). The ferroelectric measurements of the thin films show *E–P* hysteresis loops at room temperature ($T_c = 28.0\,°C$) with remnant polarization of $0.022\ \mu C\,cm^{-2}$ and a coercive field of $25\ kV\,cm^{-1}$.

Ferroelectric Materials

X.-L. Li, K. Chen, Y. Liu, Z.-X. Wang, T.-W. Wang, J.-L. Zuo, Y.-Z. Li, Y. Wang, J. S. Zhu, J.-M. Liu, Y. Song,* X.-Z. You* ______ **6820 – 6823**

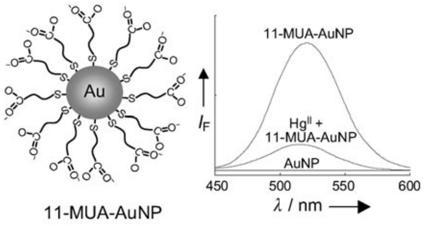
Molecule-Based Ferroelectric Thin Films: Mononuclear Lanthanide Enantiomers Displaying Room-Temperature Ferroelectric and Dielectric Properties

Fluorescent Nanoparticles

C.-C. Huang, Z. Yang, K.-H. Lee, H.-T. Chang* ———— **6824 – 6828**

Synthesis of Highly Fluorescent Gold Nanoparticles for Sensing Mercury(II)

Quenching upon aggregation: 11-Mercaptoundecanoic acid (11-MUA)-protected Au nanoparticles (11-MUA-AuNPs) are much more stable and fluoresce much more strongly than the corresponding unmodified AuNPs. After addition of 2,6-pyridinedicarboxylic acid, the 11-MUA-AuNPs bind to Hg^{II} with both high sensitivity and selectivity.

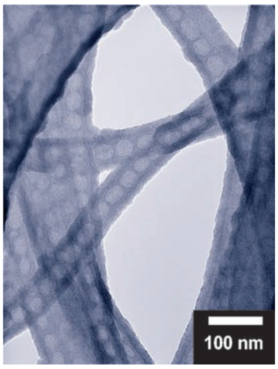


Functionalized Nanowires

X. Chen,* M. Knez, A. Berger, K. Nielsch, U. Gösele, M. Steinhart* — **6829 – 6832**

Formation of Titania/Silica Hybrid Nanowires Containing Linear Mesocage Arrays by Evaporation-Induced Block-Copolymer Self-Assembly and Atomic Layer Deposition

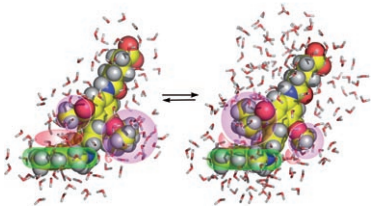
Hot-wired silica: Titania-functionalized silica nanowires containing linear arrays of mesocages (see picture) are prepared by a combination of evaporation-induced self-assembly of polystyrene-*block*-poly(ethylene oxide) soft templates inside nanoporous hard templates and atomic layer deposition. This combination allows the independent tuning of the internal fine structure of the nanowires and the properties of their outer surface.



Molecular Folding

B. Bhayana, C. S. Wilcox* — **6833 – 6836**

A Minimal Protein Folding Model To Measure Hydrophobic and CH–π Effects on Interactions between Nonpolar Surfaces in Water



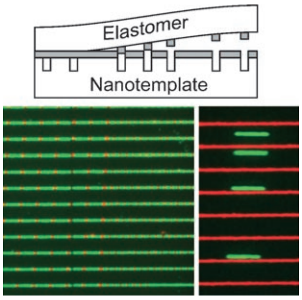
In the balance: A synthetic molecule that exhibits two-state folding behavior in water is described. Quantitative experiments reveal that the microscopic hydrophobic effect is similar in magnitude to the CH–π interaction. These forces may therefore be equally important in the folding of aromatic-rich regions of proteins. The method allows a new approach to the direct measurement of excess surface energy associated with nonpolar surfaces.

Nanolithography

S. R. Coyer, A. J. García, E. Delamarche* ———— **6837 – 6840**

Facile Preparation of Complex Protein Architectures with Sub-100-nm Resolution on Surfaces

Ink, subtract, print: A novel method is developed for patterning proteins into complex architectures with high resolution, high contrast, and self-alignment (see fluorescence micrographs). An elastomer is inked with proteins, and a nanotemplate is used to selectively subtract proteins, leaving a pattern that is then printed onto a substrate.

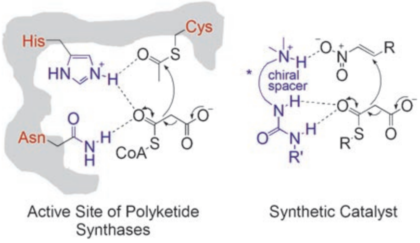


Organocatalysis

J. Lubkoll, H. Wennemers* — 6841 – 6844

Mimicry of Polyketide Synthases—Enantioselective 1,4-Addition Reactions of Malonic Acid Half-Thioesters to Nitroolefins

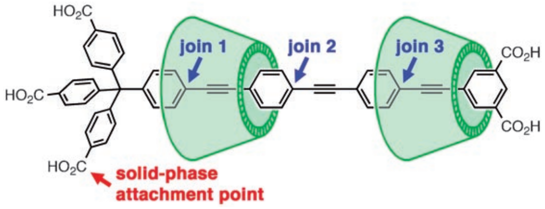
Bifunctionality is the key for mimicking the active site of polyketide synthases with synthetic metal-free organocatalysts (see picture). Cinchona alkaloid derivatives bearing both a basic site and a urea moiety catalyze conjugate enantioselective addition reactions of malonic acid half thioesters (MAHTs) to nitroolefins with up to quantitative yields and selectivities up to 90% *ee*.



Rotaxane Synthesis

H. W. Daniell, E. J. F. Klotz, B. Odell,
T. D. W. Claridge,
H. L. Anderson* — 6845 – 6848

Solid-Phase Synthesis of Oligo(phenylene ethynylene) Rotaxanes



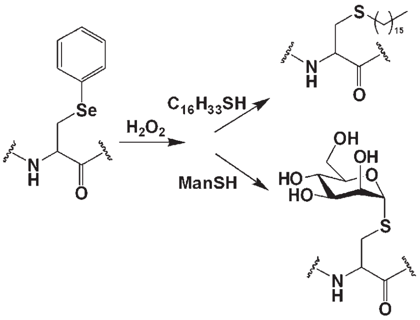
Hooks and feelers: The use of a bulky tripod-shaped stopper as a solid-phase attachment point proves essential for the controlled iterative solid-phase synthesis of an α-cyclodextrin [3]rotaxane (see picture). NMR spectroscopy confirms the structure and shows that both the cyclodextrin units have well-defined locations and orientations.

Nonnatural Amino Acids

J. Wang, S. M. Schiller,
P. G. Schultz* — 6849 – 6851

A Biosynthetic Route to Dehydroalanine-Containing Proteins

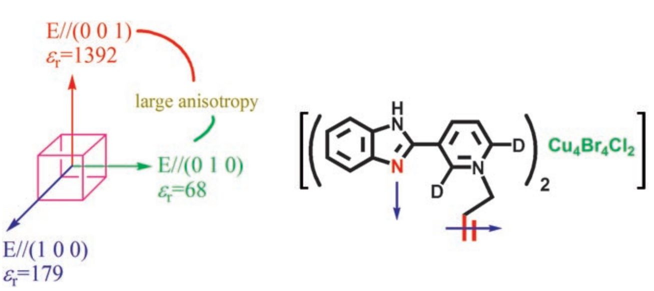
It's not natural: The nonnatural amino acid phenylselenocysteine has been genetically incorporated into proteins in *E. coli* in response to the amber nonsense codon TAG. Oxidative elimination followed by Michael addition led to incorporation of (*S*)-hexadecyl- and (*S*)-mannosylcysteine into green fluorescent protein. This approach provides a useful method to modify protein side chains and backbone structures.



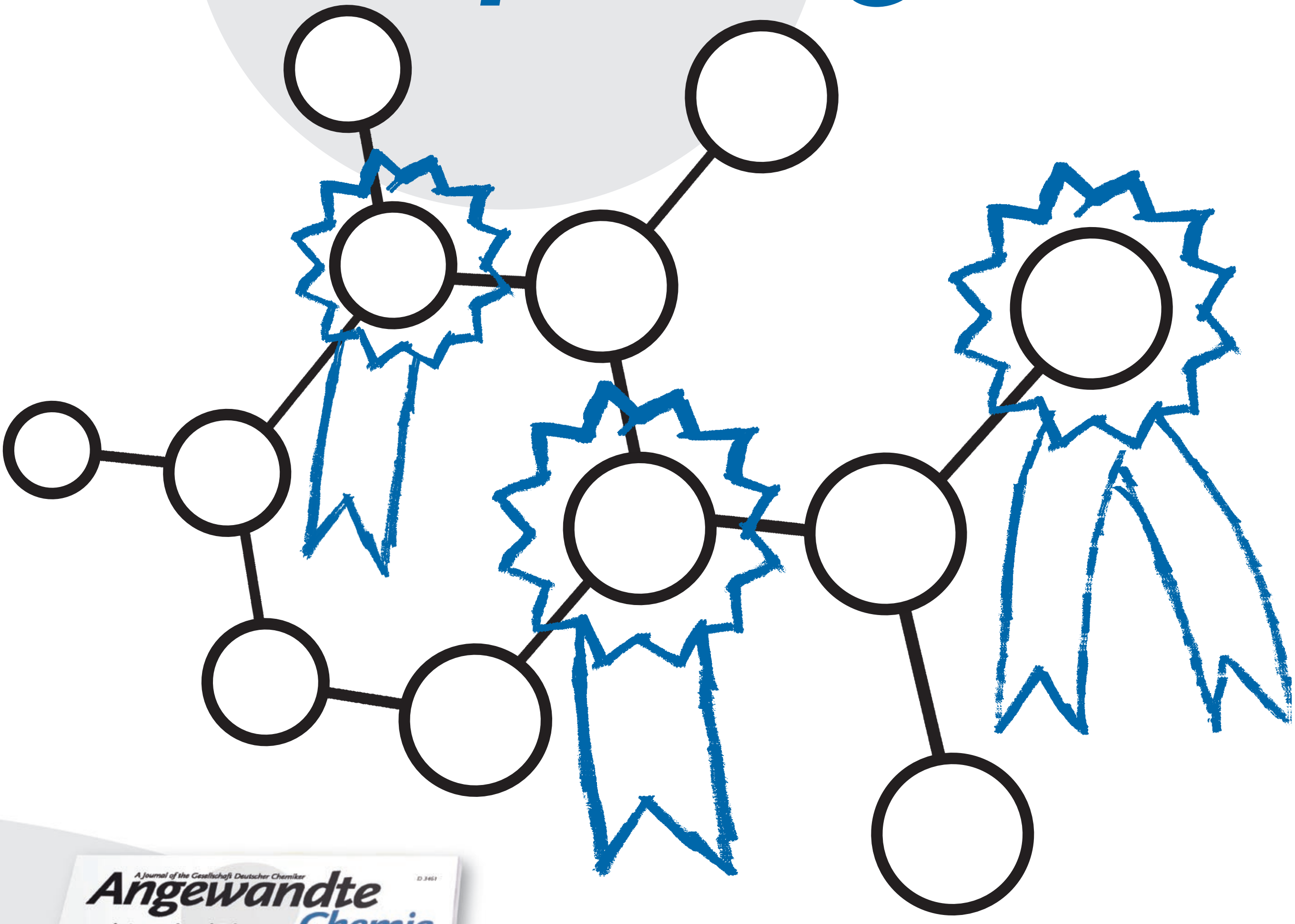
Anisotropy

Q. Ye, H. Zhao, Z.-R. Qu, D.-W. Fu,
R.-G. Xiong,* Y.-P. Cui,* T. Akutagawa,*
P. W. H. Chan,
T. Nakamura* — 6852 – 6856

Large Anisotropy and Effect of Deuteration on Permittivity in an Olefin Copper(I) Complex



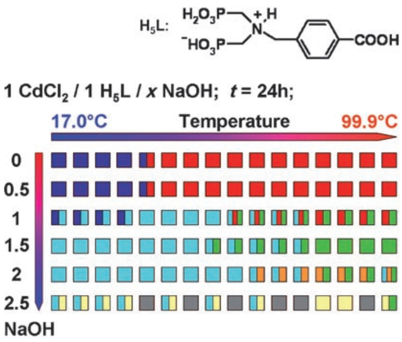
Different directions: Huge and permanent anisotropy (see picture, left) was observed in an olefin copper complex (see structural formula, right). This phenomenon is likely due to weak D···Br interactions in the crystal.



High-Throughput Methods

S. Bauer, N. Stock* ______ 6857 – 6860

Implementation of a Temperature-Gradient Reactor System for High-Throughput Investigation of Phosphonate-Based Inorganic–Organic Hybrid Compounds

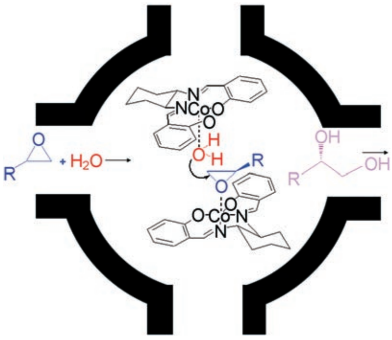


Five new Cd phosphonates were discovered in a systematic investigation of the influence of the reaction temperature besides composition and pH value on the synthesis of inorganic–organic hybrid compounds in the $CdCl_2/H_5L/NaOH$ system, which was achieved by the title procedure. In the resulting crystallization diagram (see picture), each color corresponds to a different phase.

Heterogeneous Catalysis

H. Q. Yang, L. Zhang, L. Zhong, Q. H. Yang,* C. Li* ______ 6861 – 6865

Enhanced Cooperative Activation Effect in the Hydrolytic Kinetic Resolution of Epoxides on [Co(salen)] Catalysts Confined in Nanocages



Being cagey: More than two chiral [Co(salen)] catalyst molecules can be confined in one nanocage of SBA-16 by reducing the pore entrance size by silylation. The [Co(salen)]/SBA-16 catalysts with more than two [Co(salen)] complexes in each cage show a significantly enhanced cooperative activation effect and exhibit much higher activity than the homogeneous [Co(salen)] catalyst in the hydrolytic kinetic resolution of epoxides (see scheme).

Combustion Chemistry

X. Gu,* F. Zhang,* Y. Guo,* R. I. Kaiser* ______ 6866 – 6869

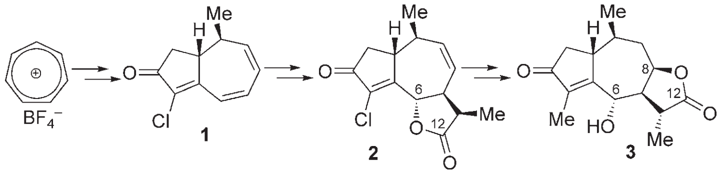
Crossed-Molecular-Beam Study on the Formation of Phenylacetylene from Phenyl Radicals and Acetylene

A hot topic! Crossed-molecular-beam experiments showed that phenylacetylene molecules—precursors to polycyclic aromatic hydrocarbons in combustion flames and in carbon-rich planetary nebulae—can be formed through reactions of phenyl radicals with acetylene under single-collision conditions (see picture).

Natural Products

S. Carret, J.-P. Deprés* ______ 6870 – 6873

Access to Guaianolides: Highly Efficient Stereocontrolled Total Synthesis of (±)-Geigerin



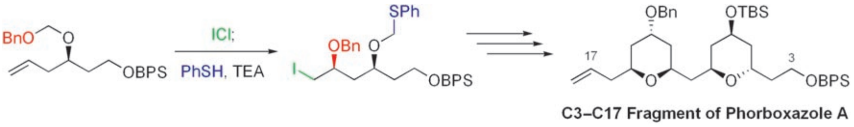
Geiger counter: The first total synthesis of geigerin (**3**), a member of the guaian-8,12-olides, has been achieved in eight regio- and stereocontrolled steps from the tropylium cation. En route, the guaian-6,12-olide **2** is formed in two steps from the hydroazulenone **1**, a versatile intermediate.

Contents

Ether Transfer

R. Kartika, R. E. Taylor* —— **6874 – 6877**

Electrophile-Induced Ether Transfer: Stereoselective Synthesis of 2,4,6-Trisubstituted Tetrahydropyrans



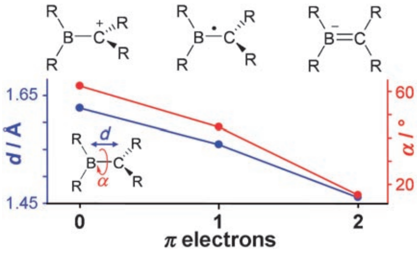
A negative attack: Synthesis of 4-alkoxy-2,6-*cis*- and its stereocomplementary 4-alkoxy-2,6-*trans*-tetrahydropyrans has been achieved in high yield and with excellent stereocontrol by a common strategy: electrophile-induced ether-transfer, cyclization, and functionalization reactions (see scheme; Bn = benzyl; BPS = *tert*-butyldiphenylsilyl; TBS = *tert*-butyldimethylsilyl; TEA = triethylamine).

Multiple Bonding

C.-W. Chiu, F. P. Gabbaï* — **6878 – 6881**

Structural Changes Accompanying the Stepwise Population of a B–C π Bond

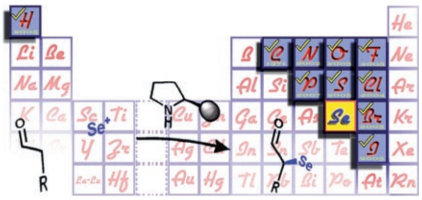
Get Shorty: The central boron–carbon bond of an α-borylated carbocation undergoes a noticeable shortening upon reduction by one and two electrons, and the degree of twisting about this bond is also noticeably reduced (see graph). According to both experiment and theory, these effects result from the sequential population of the central boron–carbon π bond.



Asymmetric Organocatalysis

M. Tiecco, A. Carlone, S. Sternativo, F. Marini,* G. Bartoli, P. Melchiorre* ———— **6882 – 6885**

Organocatalytic Asymmetric α-Selenenylation of Aldehydes



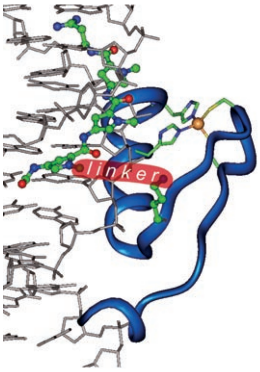
Getting round the (periodic) table: The enamine activation concept has been extended to the asymmetric addition of selenium-based compounds to aldehydes in an organocatalytic transformation that provides high reaction efficiency and stereocontrol (*ee* values ranging from 95 to 99%) with readily available chiral secondary amines. The chiral α-seleno aldehydes thus formed can be used as versatile intermediates .

Zinc-Finger Motifs

O. Vázquez, M. E. Vázquez, J. B. Blanco, L. Castedo, J. L. Mascareñas* ——— **6886 – 6890**

Specific DNA Recognition by a Synthetic, Monomeric Cys_2His_2 Zinc-Finger Peptide Conjugated to a Minor-Groove Binder

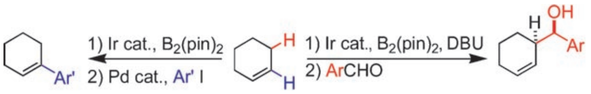
Wrapped around the finger: Tailored Cys_2His_2 zinc-finger domains can specifically bind to DNA when assisted by minor-groove accessory interactions. In this way, appropriately designed hybrids containing the zinc-finger unit of the GAGA factor and a distamycin-like tripyrrole bind with high affinity to DNA sites that have a GAG triad near the 3′ side of an A-rich fragment.



C–H Activation

V. J. Olsson, K. J. Szabó* ____ 6891 – 6893

Selective One-Pot Carbon–Carbon Bond Formation by Catalytic Boronation of Unactivated Cycloalkenes and Subsequent Coupling

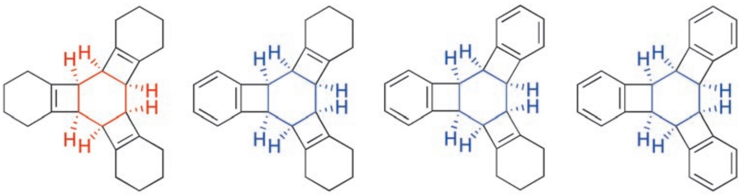


Two channels: Cycloalkenes can be selectively functionalized by iridium-catalyzed boronation followed by Suzuki coupling with an aryl iodide or reaction with an aldehyde. The selectivity for allylic and vinylic functionalization can be controlled by a slight change of the reaction conditions. DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene, pin = pinacol.

Cycloreversion

M. J. Eichberg, K. N. Houk, J. Lehmann, P. W. Leonard, A. Märker, J. E. Norton, D. Sawicka, K. P. C. Vollhardt,* G. D. Whitener, S. Wolff ____ 6894 – 6898

The Thermal Retro[2+2+2]cycloaddition of Cyclohexane Activated by Triscyclobutenannelation: Concerted All-Disrotatory versus Stepwise Conrotatory Pathways to Fused [12]Annulenes



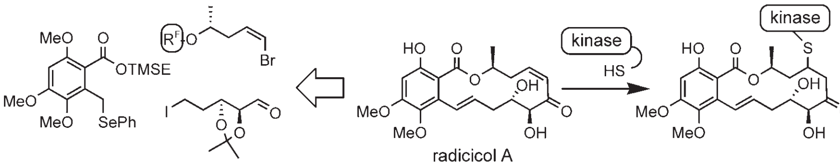
1 2 3 4

All dis or all con? While benzo analogues **2**–**4** undergo cycloreversion of the central cyclohexane ring by all-disrotatory opening, the triscyclobutenocyclohexane **1** does so by stepwise conrotatory cyclobutane rupture. This remarkable conclusion is based on DFT calculations carried out in conjunction with experiments.

Total Synthesis

P.-Y. Dakas, S. Barluenga, F. Totzke, U. Zirrgiebel, N. Winssinger* ____ 6899 – 6902

Modular Synthesis of Radicicol A and Related Resorcylic Acid Lactones, Potent Kinase Inhibitors

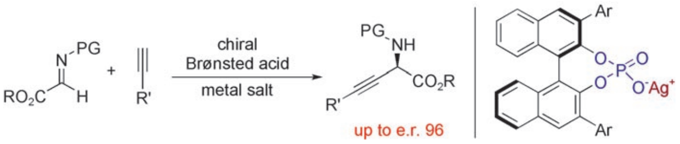


Short and sweet: A concise and modular synthesis of radicicol A and related resorcylic acid lactones using fluorous isolation technology and immobilized reagents is reported (see scheme, $R^F = C_3H_6C_6F_{13}$, TMSE = 2-(trimethylsilyl)-ethyl). The compounds are found to be potent (low-nanomolar) inhibitors of selected kinases. Despite their irreversible inactivation of kinases, they show good selectivity amongst a panel of 127 kinases.

Enantioselective Catalysis

M. Rueping,* A. P. Antonchick, C. Brinkmann ____ 6903 – 6906

Dual Catalysis: A Combined Enantioselective Brønsted Acid and Metal-Catalyzed Reaction—Metal Catalysis with Chiral Counterions



Double take: The combination of enantioselective Brønsted acid catalyzed activation and metal-catalyzed alkynylation of α-imino esters under mild reaction conditions leads to amino acids in high yields and with excellent e.r. values (see scheme; PG = protecting group).

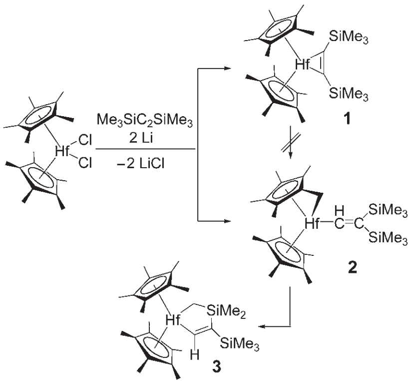
VIP

Unusual Bond Activations

T. Beweries, V. V. Burlakov, M. A. Bach, S. Peitz, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal,* B. Pathak, E. D. Jemmis* ______ 6907 – 6910

Tandem Si–C and C–H Activation for Decamethylhafnocene and Bis(trimethylsilyl)acetylene

Hafnium's triumph over titanium and zirconium! Unusual tandem Si–C and C–H bond activations by hafnium to form the alkenyl complex **2** and the silahafnacyclopentene **3** were observed in the reaction of decamethylhafnocene and bis(trimethylsilyl)acetylene. The higher reactivity of hafnocene compounds relative to their titanocene and zirconocene congeners is of general importance for synthesis and catalytic applications.

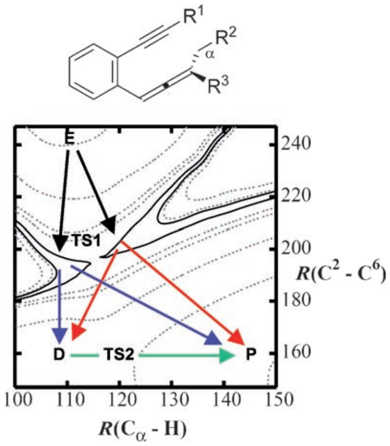


Reaction Mechanisms

M. Schmittel,* C. Vavilala, R. Jaquet ______ 6911 – 6914

Elucidation of Nonstatistical Dynamic Effects in the Cyclization of Enyne Allenes by Means of Kinetic Isotope Effects

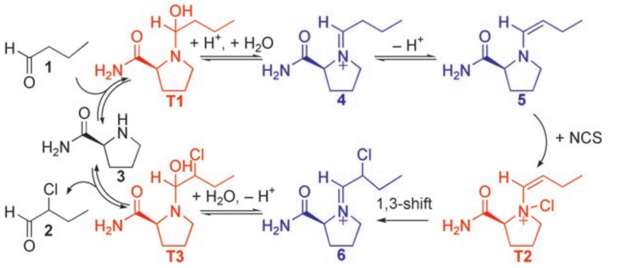
In no man's land—a reaction without a classic mechanism: A series of enyne allenes follow neither the classical concerted nor stepwise mechanism but rather comply with dynamic nonstatistical laws. The computed potential energy surface (see figure) and experimental kinetic isotope effects indicate that dynamic effects operate before as well as after the transition state.



Organocatalytic Halogenation

C. A. Marquez, F. Fabbretti, J. O. Metzger* ______ 6915 – 6917

Electrospray Ionization Mass Spectrometric Study on the Direct Organocatalytic α-Halogenation of Aldehydes



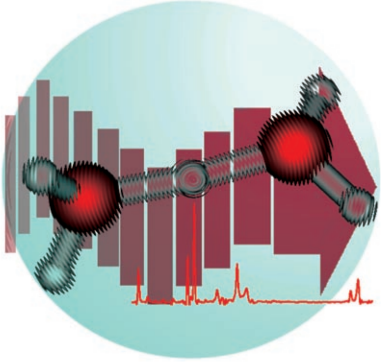
Halide effects: A mechanistic study on the L-prolineamide-catalyzed α-halogenation of butanal **1** by ESI-MS has enabled the direct detection of the most important intermediates in the catalysis cycle, including the reactive N–Cl intermediate (**T2** in scheme). In contrast, the reaction with *N*-bromo- and *N*-iodosuccinimide occurs by direct C halogenation.

Hydrated Proton

O. Vendrell, F. Gatti,
H.-D. Meyer* ———— 6918–6921

Dynamics and Infrared Spectroscopy of the Protonated Water Dimer

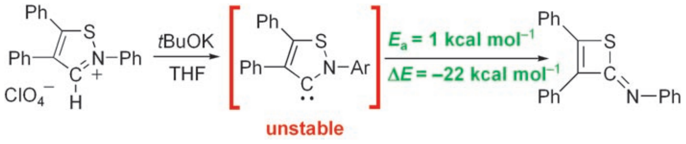
Coupling shakes this couple: Dynamics and the IR absorption spectrum of the protonated water dimer are reported by full-dimensional quantum simulation. Strong couplings between the IR-active proton-transfer motion and low-frequency, large-amplitude torsional modes are clearly identified, and their role in the cluster dynamics is explained. These couplings are responsible for the characteristic doublet at about 1000 cm^{-1}.



Singlet Carbenes

A. DeHope, V. Lavallo, B. Donnadieu,
W. W. Schoeller,
G. Bertrand* ———— 6922–6925

Recently Reported Crystalline Isothiazole Carbenes: Myth or Reality



Singlet carbenes are not always stable: Isothiazole carbenes, recently reported as crystalline solids, cannot even be observed at room temperature; they rearrange into their 2-imino-2*H*-thiete isomers with an energy barrier of about 1 kcal mol^{-1} (see scheme). See also the following Correspondence.

Correspondence

Singlet Carbenes

J. Wolf, W. Böhlmann, M. Findeisen,
T. Gelbrich,
H.-J. Hofmann, B. Schulze* ———— 6926

Reply to "Recently Reported Crystalline Isothiazole Carbenes: Myth or Reality"

In light of the results of Bertrand and coworkers, the isothiazole carbenes previously reported by us cannot be considered to be stable. Evidently they are intermediates, which rapidly isomerize to the 2-imino-2*H*-thiete isomers. Nevertheless, it is possible to obtain their dimers and to postulate their contribution in the formation of morpholino or piperidino derivatives.

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).

Service

Spotlights Angewandte's Sister Journals ———— *6762–6763*

Keywords ———— *6928*

Authors ———— *6929*

Preview ———— *6931*