Contents

VIP *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:*

*P. Mukhopadhyay, G. Zuber, P. Wipf, D. N. Beratan**
Contribution of a Chiral Solvent Imprint of a Solute to Optical Rotation

J. Fölling, V. Belov, R. Kunetsky, R. Medda, A. Schönle, A. Egner, C. Eggeling, M. Bossi, S. Hell**
Photochromic Rhodamines Provide Fluorescence Nanoscopy with Optical Sectioning

*O. Vendrell, F. Gatti, H.-D. Meyer**
Dynamics and Infrared Spectroscopy of the Protonated Water Dimer

*J. L. Stymiest, G. Dutheuil, A. Mahmood, V. K. Aggarwal**
Lithiated Carbamates: Chiral Carbenoids for Iterative Homologation of Boranes and Boronic Esters

M. Stępień, L. Latos-Grażyński, N. Sprutta, P. Chwalisz, L. Szterenberg*
Expanded Porphyrin With a Split Personality: A Hückel–Möbius Aromaticity Switch

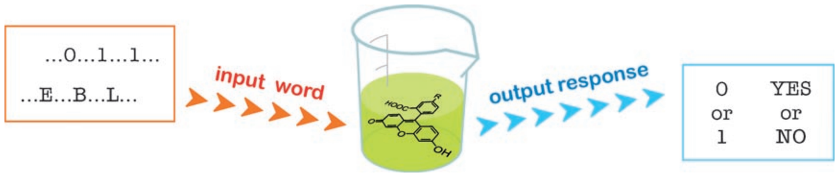
*Z. Su, Y. Xu**
Hydration of a Chiral Molecule: The Gas-Phase Study of the Propylene Oxide–(Water)$_2$ Ternary Cluster

News

Books

Highlights

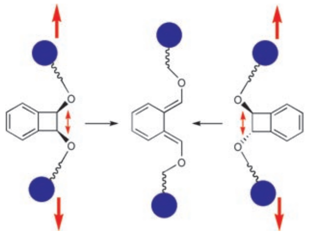
Molecular Logic



It's logical! Molecular logic gates and circuits process chemical or physical inputs according to programmed Boolean logic functions. The integration of functions within individual molecules allows complex operations, as demonstrated by a recently reported molecular keypad access device (see picture).

Ultrasound

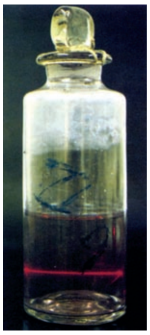
Sound bubbles: Their collapse induces mechanical stress that can be transmitted to a target single bond by means of mechanosensitive polymers attached to the two sides of a benzocyclobutene. As surprising as it may be, ultrasound guides molecules into forbidden pathways by promoting the formation of only one isomer regardless of the starting benzocyclobutene.



Contents

Essays

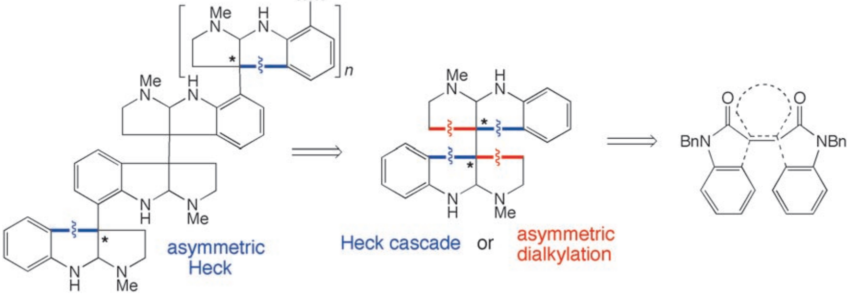
Gold Nanoparticles



"Very minute in their dimensions" is how Faraday described the metal particles present in a fine dispersion of colloidal gold upon observing its interaction with red light 150 years ago (see picture for a laser-light version of his experiment). This observation would come to serve as the basis for the modern nanoscience and nanotechnology of gold, including the use of gold nanoparticles in catalytic processes and the formation of self-assembled monolayers.

Reviews

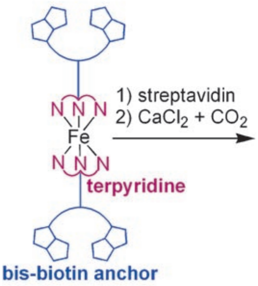
Natural Product Synthesis

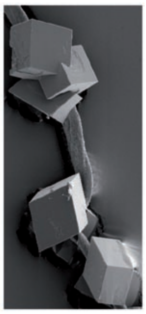


Filling the void: Efficient and flexible syntheses of many complex cyclotryptamine alkaloids are now possible because of the development of a set of stereocontrolled methods for accessing their multiple quaternary carbon stereocenters. The key steps include a cascade of Heck reactions or asymmetric dialkylation followed by an asymmetric Heck reaction (see scheme).

Communications

Coordination Polymers





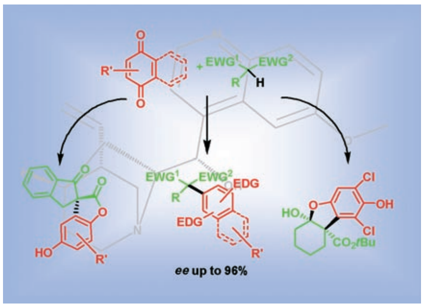
Bundle up: The introduction of streptavidin (as a linker) between two Fe^{II}(terpyridine–bis-biotin) connectors affords a one-dimensional metal–organic protein framework (MOPF). In the presence of calcium ions and CO_2 vapors, these MOPF aggregates form protein bundles that template the biomineralization of calcite.

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*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 5685/5168 (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.

Organocatalysis

J. Alemán, B. Richter,
K. A. Jørgensen* ———— 5515 – 5519

Organocatalytic Highly Enantioselective α-Arylation of β-Ketoesters

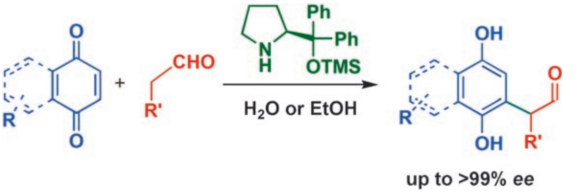


Quintessential quinones: The reaction of β-ketoesters with quinones provides a strategy to perform α-arylations, particularly when the α-aryl ring contains electron-donating groups. The reaction can be carried out enantioselectively by using cinchona alkaloids as organocatalysts and allows the synthesis of complicated polycyclic and spiro chiral compounds.

Organocatalysis

J. Alemán, S. Cabrera, E. Maerten,
J. Overgaard,
K. A. Jørgensen* ———— 5520 – 5523

Asymmetric Organocatalytic α-Arylation of Aldehydes

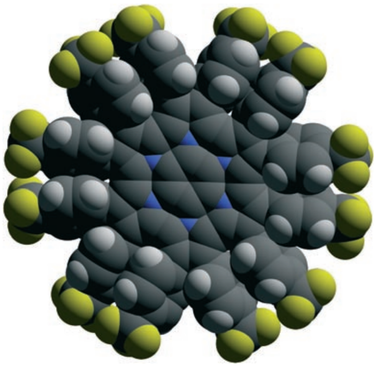


Quinone pro quo: The organocatalytic enantioselective α-arylation of aldehydes using quinones as the aromatic partner was carried out. The reaction proceeds well using H_2O or EtOH/H_2O mixtures as solvent. The corresponding optically active α-arylated aldehydes are obtained in high yields and with excellent enantioselectivities (see scheme; TMS: trimethylsilyl).

Extended π Systems

M. Takase, V. Enkelmann, D. Sebastiani,
M. Baumgarten, K. Müllen* 5524 – 5527

Annularly Fused Hexapyrrolohexaazacoronenes: An Extended π System with Multiple Interior Nitrogen Atoms Displays Stable Oxidation States

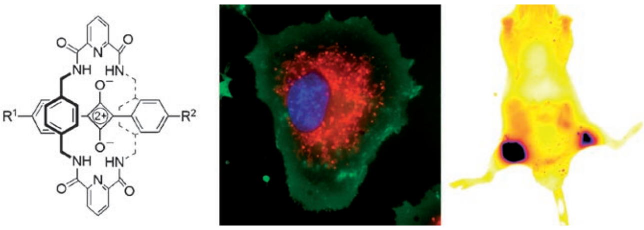


The heteroatom-stabilized annularly fused hexapyrrolohexaazacoronene shown (N blue, F green) was synthesized and isolated as a representation of a new class of nitrogen-containing molecules with extended π systems. The reversible redox behavior, a consequence of the interior N atoms, hints at potential applications in organic electronics.

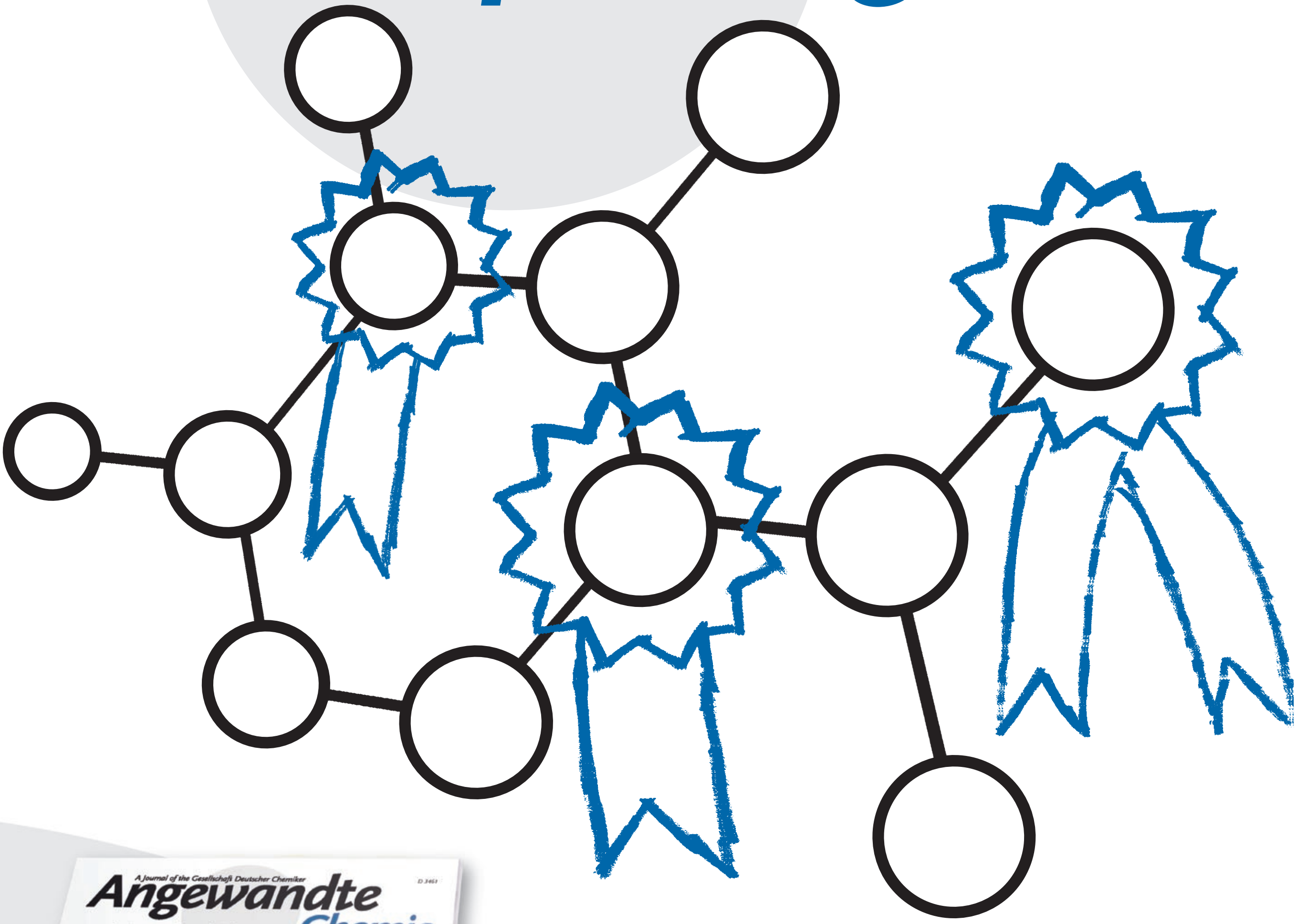
Imaging Probes

J. R. Johnson, N. Fu, E. Arunkumar,
W. M. Leevy, S. T. Gammon,
D. Piwnica-Worms,
B. D. Smith* ———— 5528 – 5531

Squaraine Rotaxanes: Superior Substitutes for Cy-5 in Molecular Probes for Near-Infrared Fluorescence Cell Imaging



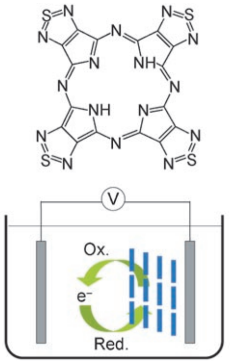
It's hip to be square: Squaraine rotaxanes have very similar photophysical properties to the commonly used Cy-5 fluorophore, but are substantially more photostable and resist self-quenching upon aggregation. Molecular probes containing squaraine rotaxanes (see structure) are shown to be versatile, high-performance NIR fluorescence stains for in vitro fluorescence imaging of cells (middle) and in vivo whole-body imaging of living mice (right).



Organic Thin Films

Y. Miyoshi, M. Kubo, T. Fujinawa, Y. Suzuki, H. Yoshikawa, K. Awaga* ____ 5532 – 5536

Electrochromism and Stable n-Type Doping of Highly Oriented Thin Films of Tetrakis(thiadiazole)porphyrazine

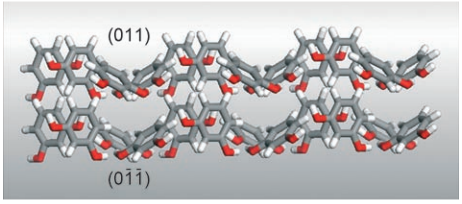


Reduced and reoxidized: Thin films (100 nm) of tetrakis(thiadiazole)porphyrazine (see picture) are highly ordered in an unusual orientation of the molecular planes owing to the strong self-assembling ability of these crystals. Electrochemical reduction of the thin films induces reversible electrochromism and n-type carrier doping.

Molecular Dynamics

J. Anwar,* J. Chatchawalsaisin, J. Kendrick ____ 5537 – 5540

Asymmetric Crystal Growth of α-Resorcinol from the Vapor Phase: Surface Reconstruction and Conformational Change Are the Culprits

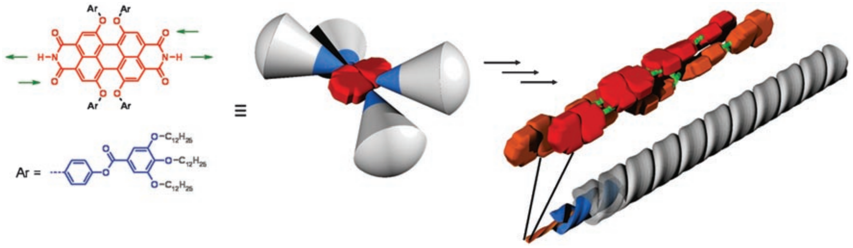


Differential growth: The growth of crystals of α-resorcinol (see picture; C gray, H white, O red) from the vapor phase is asymmetric along the polar axis. By means of molecular-dynamics simulations, the slower growth at the (011) polar surface is traced back to conformational change of the molecule and to surface reconstruction, which may be a general phenomenon in polar crystals.

Self-Assembly Processes

T. E. Kaiser, H. Wang, V. Stepanenko, F. Würthner* ____ 5541 – 5544

Supramolecular Construction of Fluorescent J-Aggregates Based on Hydrogen-Bonded Perylene Dyes

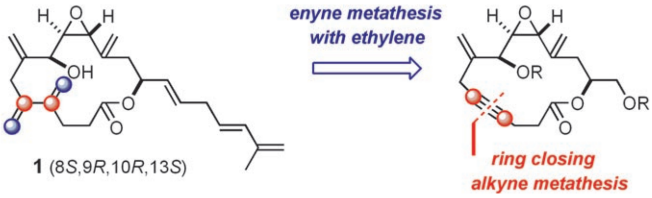


Luminous nanorods: The self-assembly of core-twisted perylene bisimide fluorophores (see structures) in nonpolar organic solvents is directed by hydrogen-bonding interactions. This supramolecular concept resulted in one-dimensional J-aggregates with a fluorescence quantum yield of near unity.

Total Synthesis

A. Fürstner,* O. Larionov, S. Flügge ____ 5545 – 5548

What is Amphidinolide V? Report on a Likely Conquest

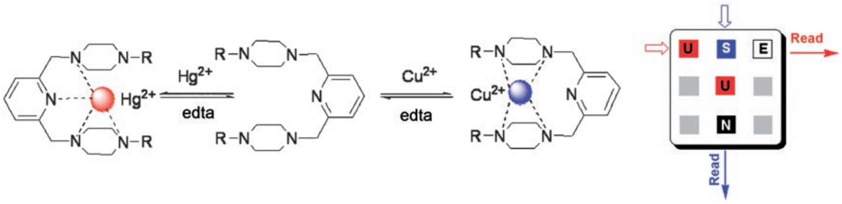


The awesome power of metathesis is reflected in the synthesis of the proposed structure of the cytotoxic natural product amphidinolide V, as well as of all other stereomers containing a *trans*-epoxide unit. It can be concluded from the comprehensive data set obtained that the 8*S*,9*R*,10*R*,13*S*-configured compound **1** most likely represents amphidinolide V, even though a single resonance in the ^{1}H NMR spectrum deviates from the reported value.

Molecular Devices

Z. Guo, W. Zhu,* L. Shen,
H. Tian* ———————— **5549 – 5553**

A Fluorophore Capable of Crossword Puzzles and Logic Memory

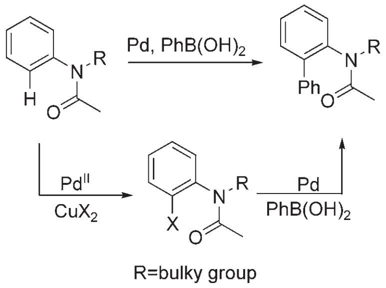


Puzzlingly logical: The characteristic fluorescence of Hg^{2+}-selective OFF-ON and Cu^{2+}-selective ON-OFF operations can be monitored and controlled reversibly by the sequence and ratio of Hg^{2+} and Cu^{2+} inputs. These inputs have been used to construct a molecular keyboard that is capable of crossword puzzles and logic memory (see picture).

Palladium Catalysis

Z. Shi,* B. Li, X. Wan, J. Cheng, Z. Fang,
B. Cao, C. Qin, Y. Wang —— **5554 – 5558**

Suzuki–Miyaura Coupling Reaction by Pd^{II}-Catalyzed Aromatic C–H Bond Activation Directed by an *N*-Alkyl Acetamino Group

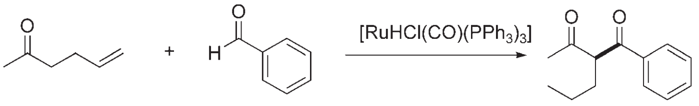


A seamless join: An efficient method to construct a $C(sp^2)-C(sp^2)$ bond has been developed by using a Suzuki–Miyaura-type coupling of *N*-alkyl acetanilides with boronic acids. The reaction was catalyzed by a Pd^{II} species and the C–H bond activation was directed by the acetamino group (see scheme). This reaction offers a halogen-free method to construct complicated structures.

Homogeneous Catalysis

T. Fukuyama, T. Doi, S. Minamino,
S. Omura, I. Ryu* ———— **5559 – 5561**

Ruthenium Hydride Catalyzed Regioselective Addition of Aldehydes to Enones To Give 1,3-Diketones



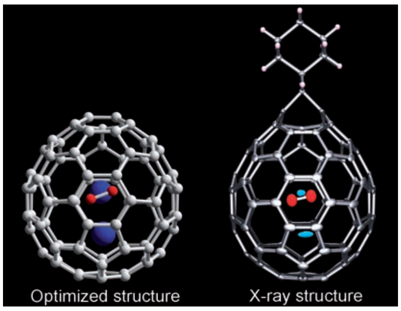
It all adds up: Straightforward access to 2-alkyl-substituted 1,3-diketones is provided by a regioselective addition of aldehydes to enones catalyzed by the ruthenium hydride catalyst $[RuHCl(CO)(PPh_3)_3]$ (see scheme). The reaction involves a hydrometalation of the enone to form a metal enolate, a cross-aldol reaction to form an alkoxymetal species, and a subsequent β-metal hydride elimination.

Endohedral Fullerenes

Y. Iiduka, T. Wakahara, K. Nakajima,
T. Nakahodo, T. Tsuchiya, Y. Maeda,
T. Akasaka,* K. Yoza, M. T. H. Liu,
N. Mizorogi, S. Nagase* —— **5562 – 5564**

Experimental and Theoretical Studies of the Scandium Carbide Endohedral Metallofullerene $Sc_2C_2@C_{82}$ and Its Carbene Derivative

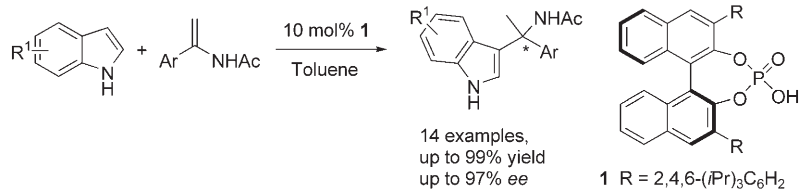
It's what's on the inside that counts: The structure of $Sc_2C_2@C_{82}$(III), as suggested by ^{13}C NMR spectroscopy and density functional calculations (see picture, left; C red and gray, Sc blue), contains two Sc and two C atoms inside the C_{82} cage. This mode of encapsulation is verified by X-ray single-crystal analysis of the cycloadduct of $Sc_2C_2@C_{82}$(III) and adamantylidene carbene (see picture, right).



Asymmetric Catalysis

Y.-X. Jia, J. Zhong, S.-F. Zhu, C.-M. Zhang, Q.-L. Zhou* **5565 – 5567**

Chiral Brønsted Acid Catalyzed Enantioselective Friedel–Crafts Reaction of Indoles and α-Aryl Enamides: Construction of Quaternary Carbon Atoms

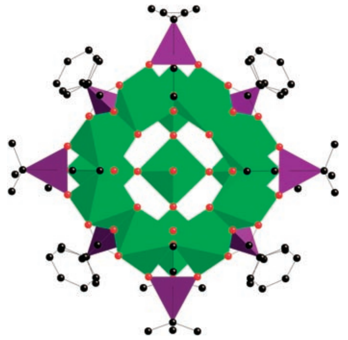


***S* express**: Quaternary carbon atoms are constructed in excellent yields with high enantioselectivities by a highly efficient chiral Brønsted acid catalyzed Friedel–Crafts reaction of indoles and α-aryl enamides (see scheme). The presence of H atoms on the N atoms of both the indole and enamide moieties is essential for the reaction to occur. The indole molecule attacks from the *Re* face to give *S*-configured products.

Vanadium(III) Compounds

S. Khanra, M. Kloth, H. Mansaray, C. A. Muryn, F. Tuna, E. C. Sañudo, M. Helliwell, E. J. L. McInnes,* R. E. P. Winpenny* **5568 – 5571**

Synthesis of Molecular Vanadium(III) Phosphonates

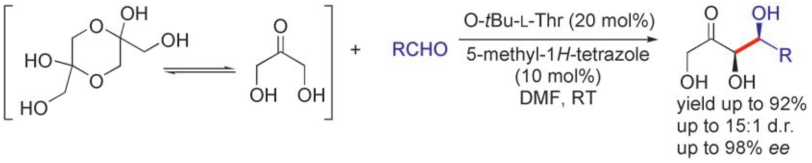


All in the family: Organophosphonate complexes of high-valent vanadium are common, but their V^{III} analogues are few and far between. Reaction of VCl$_3$ precursors and phosphonates under solvothermal conditions leads to a family of corresponding vanadium(III)-based phosphonates, including the layered $\{V^{III}_{12}(V^{IV}O)\}$ cluster shown in the picture (V green, P purple, O red, C black). Preliminary magnetic studies are also reported.

Asymmetric Catalysis

S. S. V. Ramasastry, K. Albertshofer, N. Utsumi, F. Tanaka, C. F. Barbas III* **5572 – 5575**

Mimicking Fructose and Rhamnulose Aldolases: Organocatalytic *syn*-Aldol Reactions with Unprotected Dihydroxyacetone

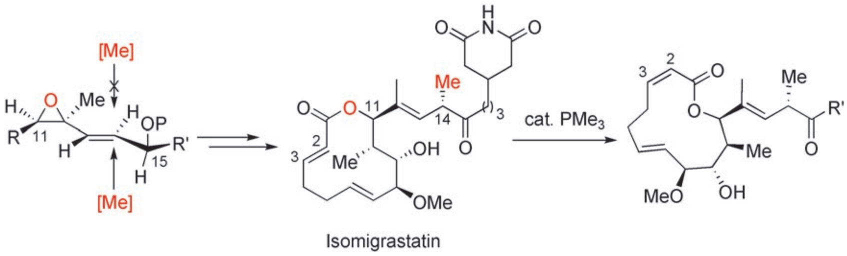


Completing the quattuorvirate: Amino acids that contain primary amines directly catalyze *syn*-selective asymmetric aldol reactions between unprotected dihydroxyacetone and a variety of aromatic and aliphatic aldehydes (see scheme). This new strategy provides the organocatalytic mimics of the L-rhamnulose 1-phosphate and D-fructose 1,6-diphosphate aldolases.

Natural Product Synthesis

I. J. Krauss, M. Mandal, S. J. Danishefsky* **5576 – 5579**

Total Synthesis of (+)-Isomigrastatin

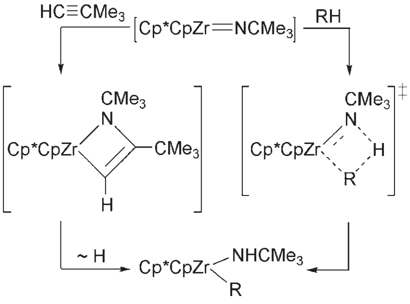


Marginally stable natural products: The asymmetric total synthesis of the hydrolytically and thermally labile natural product (+)-isomigrastatin was demonstrated. The thermodynamic instability of a 2*E*-configured double bond in the context of this 12-membered macrolide was further demonstrated by phosphine-catalyzed isomerization to the 2*Z* configuration.

C–H Activation

H. M. Hoyt, R. G. Bergman* **5580 – 5582**

Kinetic Control and Multiple Mechanisms for C–H Bond Activation by a Zr=N Complex

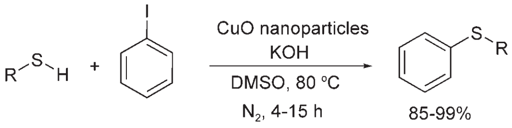


The [Cp*CpZr=NCMe$_3$(thf)] system provides the first direct measurement of kinetic selectivity in sp, sp^2, and sp^3 C–H bond activation with Group 4 imido complexes. This feature allows the design of selectivity and mechanistic experiments to probe the 1,2-RH-addition event. Substrates reacting with the highest relative rates generally form the most thermodynamically stable products. Cp* = η^5-C$_5$Me$_5$, Cp = η^5-C$_5$H$_5$.

Cross-Coupling Reactions

L. Rout, T. K. Sen,
T. Punniyamurthy* ________ **5583 – 5586**

Efficient CuO-Nanoparticle-Catalyzed C–S Cross-Coupling of Thiols with Iodobenzene



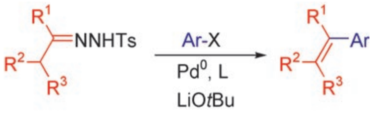
Cheap but good: Readily available CuO nanoparticles are not only less expensive than other catalysts used for the C–S cross-coupling of thiols with aryl halides, but they are also effective at a moderate temperature and low concentration. The title reaction proceeds with a variety of alkyl and aryl thiols to give the corresponding sulfides in high yields (see scheme).

Cross-Coupling Reactions

J. Barluenga,* P. Moriel, C. Valdés,
F. Aznar ________ **5587 – 5590**

N-Tosylhydrazones as Reagents for Cross-Coupling Reactions: A Route to Polysubstituted Olefins

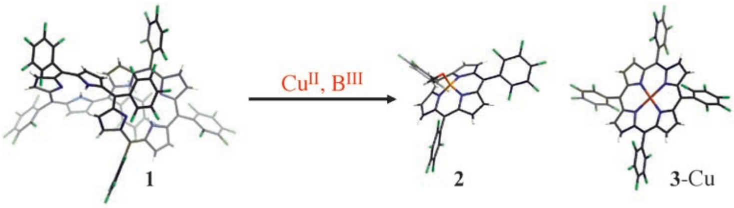
Metal-free partner: No organometallic coupling partner is required for a Pd-catalyzed cross-coupling reaction that employs *N*-tosylhydrazones as the nucleophilic component (see scheme; Ts = 4-toluenesulfonyl).



Porphyrinoid Interconversion

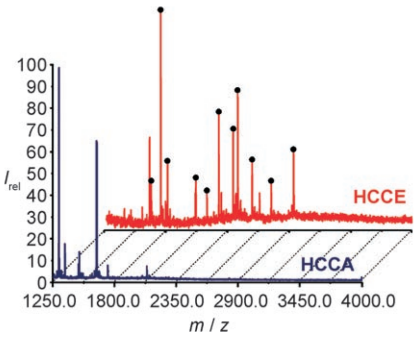
S. Saito, K. S. Kim, Z. S. Yoon, D. Kim,*
A. Osuka* ________ **5591 – 5593**

Extrusion of Boron(III) Subporphyrin from *meso*-Heptakis(pentafluorophenyl)-[32]heptaphyrin upon Cooperative Cu^{II} and B^{III} Metalation



An uneven split: Cooperative Cu^{II} and B^{III} metalation of *meso*-heptakis(pentafluorophenyl)[32]heptaphyrin (**1**) triggers an extrusion reaction to produce B^{III} *meso*-tris(pentafluorophenyl)[14]subporphyrin (**2**) along with a Cu^{II} porphyrin (**3**-Cu). Subporphyrin **2** exhibits unique optical properties that reflect the rotational restriction of its electron-withdrawing substituents.

Discrimination with a difference: The *N*-hydroxysuccinimide ester of HCCA (α-cyano-4-hydroxycinnamic acid) was used as a labeling reagent to increase the MALDI MS signal of weakly concentrated peptides of interest in a proteolytic mixture derived from cytochrome *c* relative to the signals of other peptides. The desired effect was only observed with the neutral MALDI matrix HCCE (the methyl ester of HCCA; see mass spectra).

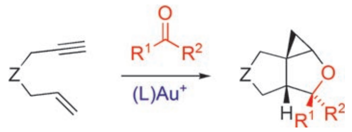


Mass Spectrometry of Proteins

D. Lascoux, D. Paramelle, G. Subra, M. Heymann, C. Geourjon, J. Martinez,* E. Forest* ______ **5594 – 5597**

Discrimination and Selective Enhancement of Signals in the MALDI Mass Spectrum of a Protein by Combining a Matrix-Based Label for Lysine Residues with a Neutral Matrix

---



Gold rush: Gold catalysis remains a highly attractive field of research for the discovery of new reaction types. A novel intermolecular addition of aldehydes and ketones to enynes leads to the diastereoselective synthesis of 2-oxabicyclo[3.1.0]hexanes (see scheme).

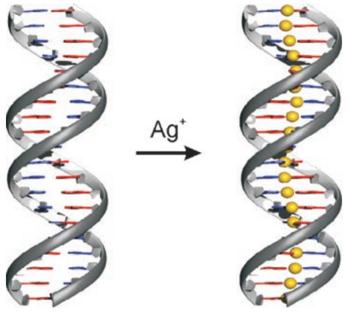
Oxabicyclohexanes

M. Schelwies, A. L. Dempwolff, F. Rominger, G. Helmchen* **5598 – 5601**

Gold-Catalyzed Intermolecular Addition of Carbonyl Compounds to 1,6-Enynes

---

Silver service: Addition of silver(I) to an oligonucleotide comprising 1-deazaadenine and thymine nucleobases leads to the formation of a Hoogsteen-type double helix with specific binding of one metal ion per base pair (see scheme). Each base pair is mediated by one hydrogen bond and by two coordination bonds.

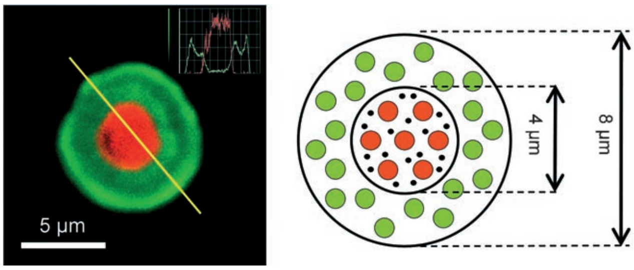


Artificial Base Pairs

F.-A. Polonius, J. Müller* ___ **5602 – 5604**

An Artificial Base Pair, Mediated by Hydrogen Bonding and Metal-Ion Binding

---



The Matryoshka theory: This unique type of shell-in-shell microcapsule facilitates the stable spatial separation of biopolymers (enzymes) within distinct compartments of a single capsule entity. Architecture and wall properties of this system allow for the concerted action of enzymes from separate capsule compartments by metabolite diffusion across a semi-permeable, intersecting polyelectrolyte membrane.

Microencapsulation

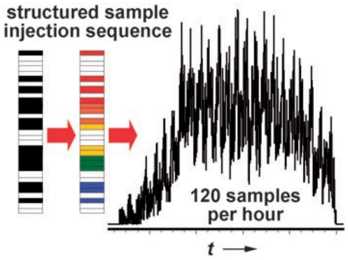
O. Kreft,* M. Prevot, H. Möhwald, G. B. Sukhorukov ______ **5605 – 5608**

Shell-in-Shell Microcapsules: A Novel Tool for Integrated, Spatially Confined Enzymatic Reactions

Analytical Methods

O. Trapp* ——— **5609–5613**

Boosting the Throughput of Separation Techniques by “Multiplexing”



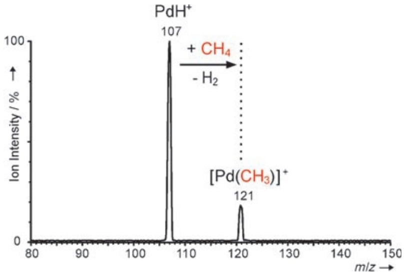
This is IT for chemical analysis: The use of structured sample injection sequences (bar codelets) in chromatography allows to increase the sample throughput by self-encoding of individual samples and mathematical deconvolution of the overlapping chromatograms (see picture). Analysis of up to 453 samples per hour could be achieved with a single separation column in gas chromatography.

Gas-Phase Reactions

M. Schlangen, H. Schwarz* **5614–5617**

Thermal Activation of Methane by Group 10 Metal Hydrides MH^+: The Same and Not the Same

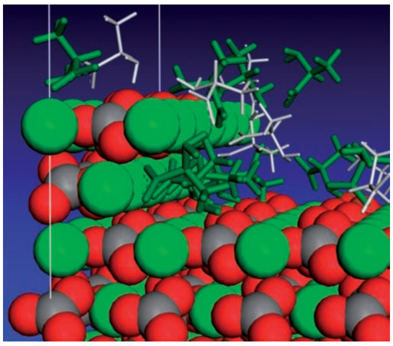
Small electronic changes matter! All three Group 10 metal hydrides MH^+ (M = Ni, Pd, Pt) bring about thermal C–H bond activation of methane, but for each system the potential energy surfaces and thus the mechanisms of the ligand exchange $MH^+ + CH_4 \rightarrow M(CH_3)^+ + H_2$ differ.



Biomineralization

S. E. Wolf, N. Loges, B. Mathiasch, M. Panthöfer, I. Mey, A. Janshoff, W. Tremel* ——— **5618–5623**

Phase Selection of Calcium Carbonate through the Chirality of Adsorbed Amino Acids

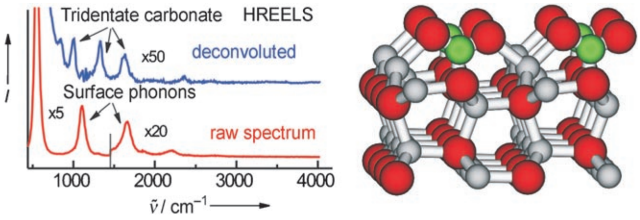


On the phase of it: The phase selection of calcium carbonate (spheres: C gray, Ca green, O red) is determined by chiral amino acids (stick models) present during the crystallization. The interplay of composition and chirality of the crystal surfaces and additives leads to enantiospecific adsorption of the D and L amino acids on chiral surface steps. The resulting surface passivation creates a kinetic barrier, which controls the phase selection.

Surface Chemistry

Y. Wang,* R. Kováčik, B. Meyer,* K. Kotsis, D. Stodt, V. Staemmler, H. Qiu, F. Traeger, D. Langenberg, M. Muhler, C. Wöll* ——— **5624–5627**

CO_2 Activation by ZnO through the Formation of an Unusual Tridentate Surface Carbonate



Greenhouse gas “al dente”: Exposure of the nonpolar $ZnO(10\bar{1}0)$ surface to CO_2 at 95 K leads to the formation of an unusual tridentate carbonate species (see picture; C green, O red, Zn gray). Use of several experimental techniques (for example, high-resolution electron energy loss spectroscopy (HREELS)) and theoretical calculations provides insight into the activation of CO_2 on the surface.

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

The issues for July 2007 appeared online on the following dates
Issue 25: June 11. · Issue 26: June 15. · Issue 27: June 22. · Issue 28: July 2

RSS Feed

Journal content prior to publication in an issue can be found online on our **Early View** page at www.angewandte.org. Stay updated on the latest journal content by registering for our **free e-mail alerts** at http://interscience.wiley.com/alerts.

Keep up with the latest research with our **RSS feed**, which provides the titles, authors, and the Digital Object Identifiers (DOIs) of Early View articles, including links to the full texts. RSS ("Really Simple Syndication") is an XML-based format for sharing and distributing web content. To receive the RSS feed, just click on the orange feed icon at www.angewandte.org, and visit http://interscience.wiley.com/rss for more information.