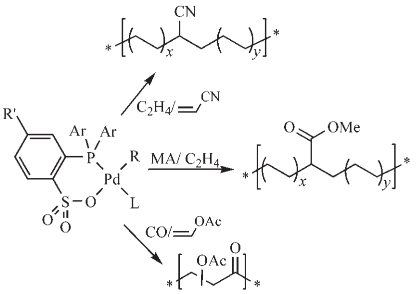
The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

News

Books

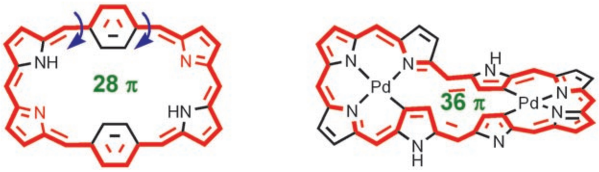
Highlights

Polymerizations



Rising to the challenge: Neutral phosphinosulfonate Pd^{II} complexes were recently demonstrated to be versatile catalysts even for the challenging insertion copolymerization of polar functionalized vinyl comonomers $H_2C{=}CHX$, such as acrylonitrile, vinyl acetate, and alkyl vinyl ethers (see scheme, MA = methyl acrylate).

Möbius Porphyrins



An interesting twist: Expanded porphyrins possess Möbius-strip-like structures in the solid state and in solution. The high conformational flexibility of individual groups enables a temperature- and solvent-dependent switch between Hückel and Möbius aromaticity. Group 10 metals can serve as clamps to stabilize the twist of the Möbius structure (see picture).

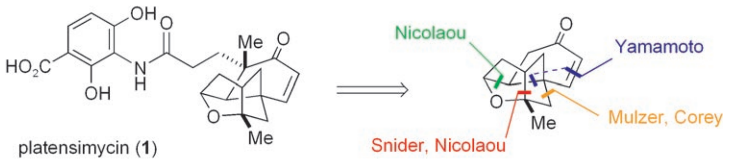
Contents

Minireviews

Natural Product Synthesis

K. Tiefenbacher, J. Mulzer* **2548 – 2555**

Synthesis of Platensimycin



platensimycin (**1**)

Route finders: The discovery of platensimycin (**1**) in 2006 has been hailed as a true breakthrough in antibiotic research. By efficiently blocking bacterial fatty acid biosynthesis it has a unique mode of action and therefore shows no cross-resistance to existing drugs. In this Minireview all the synthetic efforts towards **1** and its analogous are discussed.

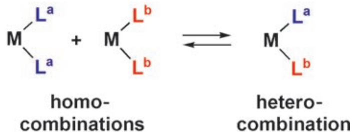
Reviews

Combinatorial Catalysis

M. T. Reetz* ____________ **2556 – 2588**

Combinatorial Transition-Metal Catalysis: Mixing Monodentate Ligands to Control Enantio-, Diastereo-, and Regioselectivity

Mix well: A novel concept in combinatorial homogeneous transition-metal catalysis lies in the mixing of two monodentate ligands in the presence of a transition metal to provide two homocombinations and one heterocombination. If the latter is most active, it will define the catalytic profile. By using this strategy, a better catalyst can be obtained without the need for preparing new ligands.



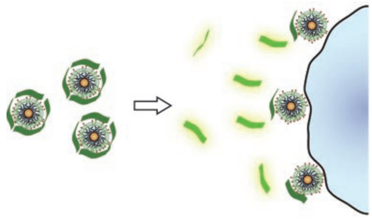
Communications

Bacteria Sensing

R. L. Phillips, O. R. Miranda,
C.-C. You, V. M. Rotello,*
U. H. F. Bunz* ____________ **2590 – 2594**

Rapid and Efficient Identification of Bacteria Using Gold-Nanoparticle–Poly(*para*-phenyleneethynylene) Constructs

Microbiological intelligence: Simple constructs of hydrophobically functionalized gold nanoarticles and a conjugated polymer (poly(*para*-phenyleneethynylene), PPE) are able to identify three different strains of *E. coli* in minutes. The negatively charged bacteria replace the negatively charged conjugated polymers from the positively charged gold nanoparticles (see scheme), differentially restoring the polymer fluorescence.



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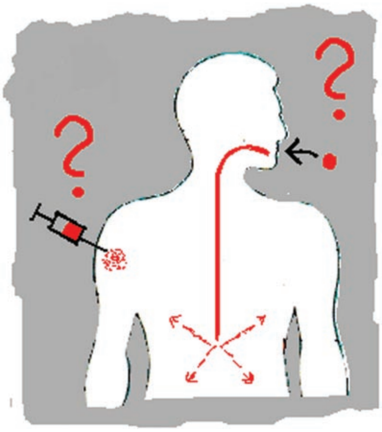
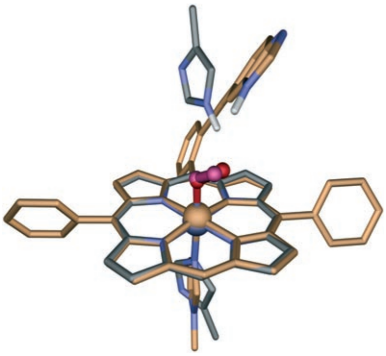
Full methyl jacket? A complete library of the N-methylated somatostatin cyclopeptidic analogue Veber–Hirschmann peptide *cyclo*(-PFwKTF-) has been prepared with the aim of improving its bioavailability. Several analogues from the library were found to bind to the somatostatin receptor in the nanomolar range and one of them shows a significant oral bioavailability of 10%. Conformational analysis shows that N-methylation is allowed at specific positions without affecting the bioactive conformation.



Drug Research

E. Biron, J. Chatterjee, O. Ovadia, D. Langenegger, J. Brueggen, D. Hoyer, H. A. Schmid, R. Jelinek, C. Gilon, A. Hoffman, H. Kessler* ___ **2595–2599**

Improving Oral Bioavailability of Peptides by Multiple N-Methylation: Somatostatin Analogues

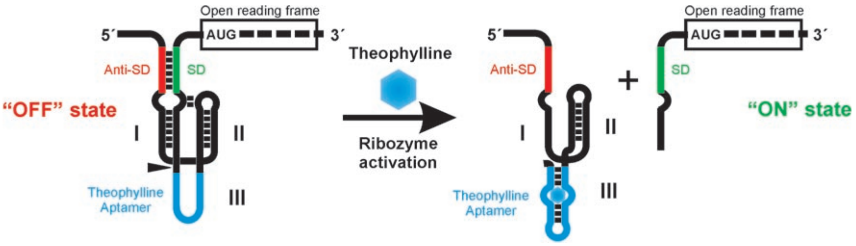


Hydrogen bond revealed: In a cobalt(II) porphyrin complex which serves as a model for the dioxygen binding site of myoglobin (Mb) and hemoglobin, a distal hydrogen bond to the bound O_2 was identified and characterized by pulse ENDOR spectroscopy. A similar but stronger hydrogen bond was revealed with the same methods in natural Co-Mb-O_2.

Hydrogen Bonds in Proteins

H. Dube, B. Kasumaj, C. Calle, M. Saito, G. Jeschke, F. Diederich* ___ **2600–2603**

Direct Evidence for a Hydrogen Bond to Bound Dioxygen in a Myoglobin/Hemoglobin Model System and in Cobalt Myoglobin by Pulse-EPR Spectroscopy



Switch-hitter: A new strategy to control gene expression relies on a ligand-dependent, ribozyme-based RNA switch. The key feature of this setup is that the ribozyme liberates the ribosome binding site upon cleavage of the message. The design made it possible to screen in vivo for an inducible aptazyme by attaching an aptamer to stem III of the ribozyme, thus preserving naturally occurring stem I/stem II contacts.

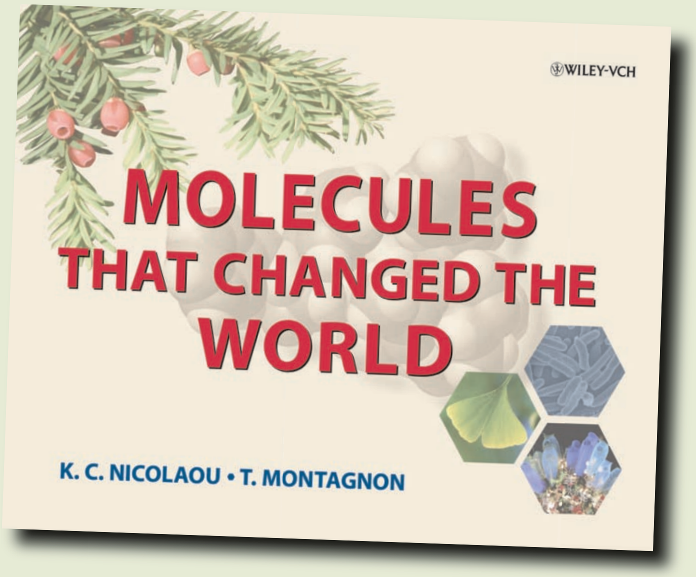
RNA Switches

M. Wieland, J. S. Hartig* ___ **2604–2607**

Improved Aptazyme Design and In Vivo Screening Enable Riboswitching in Bacteria

MOLECULES THAT CHANGED THE WORLD

K. C. Nicolaou *The Scripps Research Institute and UC San Diego, La Jolla, USA*
& **Tamsyn Montagnon** *Department of Chemistry, University of Crete, Heraklion, Crete, Greece*



ISBN: 978-3-527-30983-2
February 2008
Hardback • 385 Pages
Price £24.95 / $50.00 / €34.90

In this attractively designed book, K.C. Nicolaou introduces some of the world's **most important molecules** and engagingly demonstrates the role certain compounds play in our everyday lives as drugs, flavours or vitamins. Printed in full colour throughout and with its oversize format, this book is **a must for every chemist**, natural scientist and anyone interested in the sciences.

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- Present interesting and entertaining facts, stories and information about the people behind the scenes
- Covers 40 natural products, each of them with an enormous impact on our everyday life
- Includes a plethora of fascinating pictures

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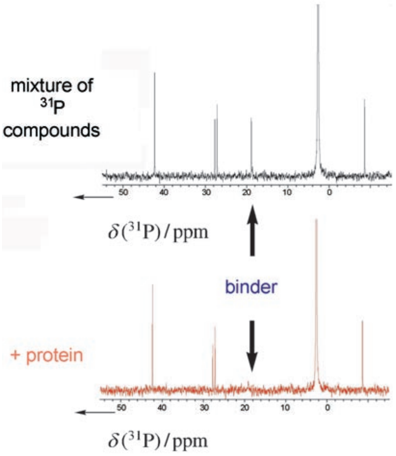
Ligand Screening

F. Manzenrieder, A. O. Frank, H. Kessler* —— 2608 – 2611

Phosphorus NMR Spectroscopy as a Versatile Tool for Compound Library Screening

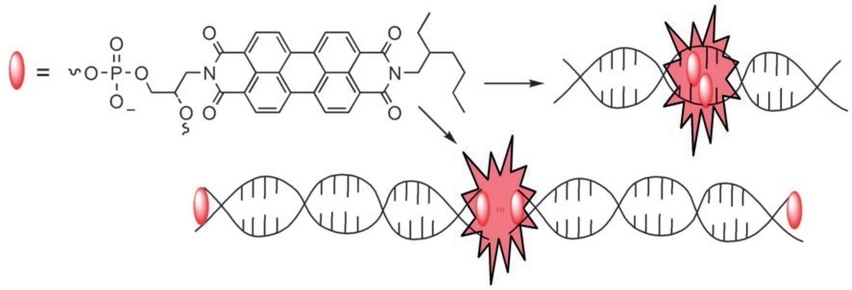


A new librarian: The applicability of NMR spectroscopy in biological and pharmaceutical research has been extended by introducing phosphorus (^{31}P) as a new nucleus for compound library screening of protein inhibitors. Several NMR-based methods, such as recovery experiments and two-dimensional measurements, were utilized to show the fundamental soundness of the newly developed ligand-based screening approach.

Fluorescent DNA

D. Baumstark, H.-A. Wagenknecht* —— 2612 – 2614

Perylene Bisimide Dimers as Fluorescent "Glue" for DNA and for Base-Mismatch Detection

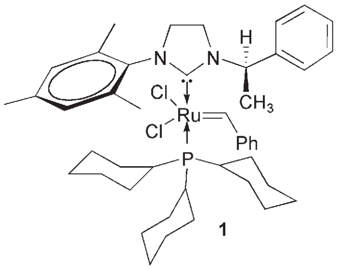


Lights up! The characteristic fluorescence of perylene bisimide dimers can be used to study DNA hybridization and DNA aggregation (see scheme) as well as the presence of single-base-pair mismatches and deletions.

Polymerization

K. Vehlow, D. Wang, M. R. Buchmeiser,* S. Blechert* —— 2615 – 2618

Alternating Copolymerizations Using a Grubbs-Type Initiator with an Unsymmetrical, Chiral N-Heterocyclic Carbene Ligand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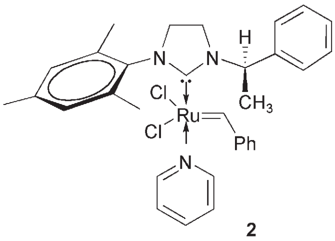
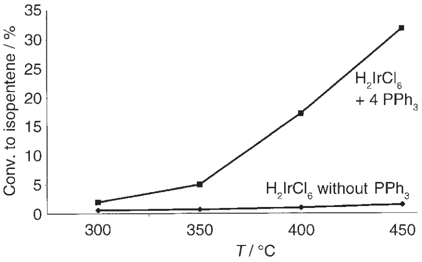

2

Good for a ROMP: Initiators **1** and **2**, which both contain an unsymmetric, chiral N-heterocyclic carbene (NHC) ligand, mediate the alternating copolymerization of norborn-2-ene with other cyclic olefins including cyclopentene and cyclooctene. The selectivity of the copolymerization is explained by the steric interaction of the growing polymer chain with the 1-phenylethyl substituent and the nitrogen atom of the NHC ligand.

Heterogeneous Dehydrogenation

H. G. Alt,* I. K. Böhmer —— 2619 – 2621

Catalytic Dehydrogenation of Isopentane with Iridium Catalysts



Activation by adding PPh_3: The catalytic dehydrogenation of isopentane to give isopentene and hydrogen with iridium catalysts on a silica gel support at 450 °C proceeds with impressive conversion when the support is impregnated with PPh_3. The active species are proposed to be iridium phosphides which arise by thermal cleavage of phenyl groups.

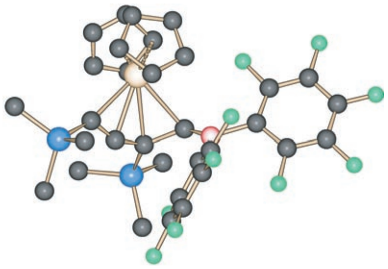
Contents

Metallacycloallenes

J. Ugolotti, G. Dierker, G. Kehr, R. Fröhlich, S. Grimme, G. Erker* ______ 2622 – 2625

Five-Membered Metallacyclic Allenoids: Synthesis and Structure of Remarkably Stable Strongly Distorted Cyclic Allene Derivatives

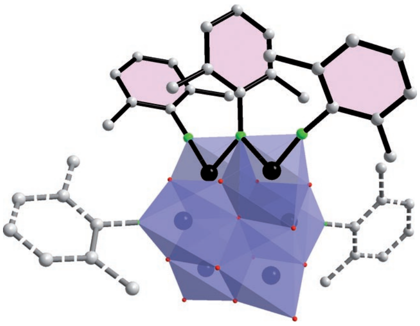
Metallocene lends a hand: Treatment of [bis(alkynyl)$HfCp_2$] complexes with $HB(C_6F_5)_2$ results in 1,1-hydroboration and subsequent carbon–carbon coupling to yield the corresponding metallacyclopenta-1,2-diene derivatives (see structure of the trimethylsilyl derivative; Hf brown, B red, Si blue, F green, C black). X-ray diffraction and a quantum chemical analysis reveal an electronic structure between a bent cyclic allene and a coordinated butenyne.



Organic–Inorganic Hybrids

J. Hao, Y. Xia, L. Wang, L. Ruhlmann,* Y. Zhu, Q. Li, P. Yin, Y. Wei,* H. Guo ______ 2626 – 2630

Unprecedented Replacement of Bridging Oxygen Atoms in Polyoxometalates with Organic Imido Ligands

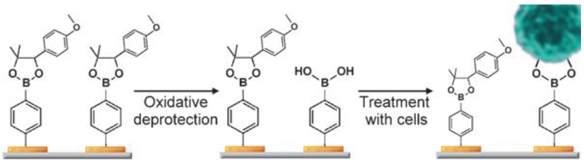


Building bridges: Two arylimido derivatives of hexamolybdate, containing unprecedented bridging imido ligands, have been synthesized and structurally characterized. Their ^1H NMR and UV/Vis spectra distinguish them from related terminally coordinated derivatives. Such compounds extend the range of organoimido polyoxometalate coordination chemistry, providing insight into the mechanism of oxo metathesis in the Lindqvist polymolybdate.

Cell Immobilization

R. Polsky, J. C. Harper, D. R. Wheeler, D. C. Arango, S. M. Brozik* 2631 – 2634

Electrically Addressable Cell Immobilization Using Phenylboronic Acid Diazonium Salts

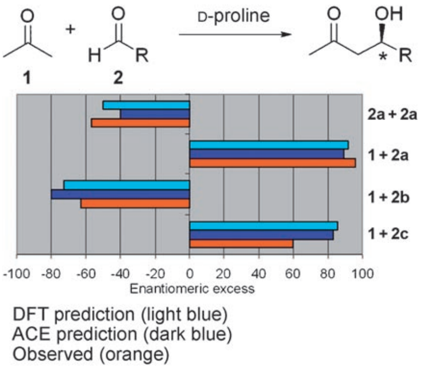


Holding cells: Individual gold electrodes can be activated by phenylboronic acid diazonium salts for the facile and reversible immobilization of eukaryotic cells (see scheme). This platform provides a simple method for on-demand release of captured cells (yeast and macrophage) and can be used in single-cell or array-based studies.

Asymmetric Synthesis

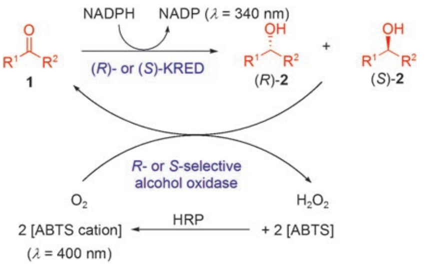
C. R. Corbeil, S. Thielges, J. A. Schwartzentruber, N. Moitessier* ______ 2635 – 2638

Toward a Computational Tool Predicting the Stereochemical Outcome of Asymmetric Reactions: Development and Application of a Rapid and Accurate Program Based on Organic Principles



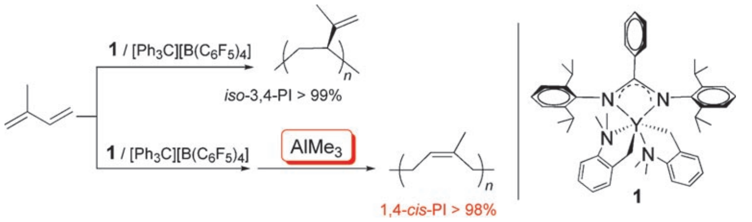
Finding an ACE in the deck: The newly developed program ACE 1.0 (ACE = asymmetric catalyst evaluation) rapidly and accurately predicts the stereochemical outcome of asymmetric reactions. Application of ACE to asymmetric Diels–Alder cycloadditions and organocatalyzed aldol reactions demonstrates high accuracy (see picture; R = *i*Pr (**2a**), Me (**2b**), Ph (**2c**)).

Biocatalysis



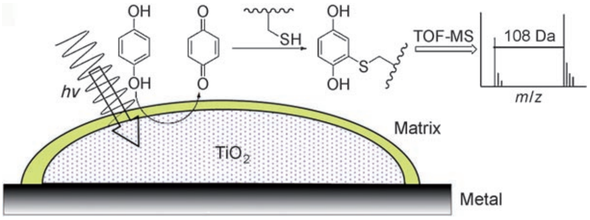
Fast and furious: A rapid and inexpensive assay for determining both the activity and enantioselectivity of ketoreductases (KREDs) has been developed (see scheme; HRP = horseradish peroxidase, ABTS = 2,2′-azino-di(3-ethyl benzthiazoline-6-sulfonic acid). This assay, which employs an enantioselective alcohol oxidase as a reporter enzyme, was used to screen a panel of 17 KREDs in only 10 min using less than 0.5 mg substrate.

Polymerization Catalysts



Aluminum switches: The addition of $AlMe_3$ to the isoprene polymerization catalyst **1**/$[Ph_3C][B(C_6F_5)_4]$ switches the regio- and stereoselectivity from 3,4-isospecific to 1,4-*cis* selective (see scheme). A heterotrinuclear Y/Al complex obtained from the reaction of **1** with $AlMe_3$ shows 1,4-*cis* selectivity under similar conditions in the presence of $[Ph_3C][B(C_6F_5)_4]$. PI = polyisoprene.

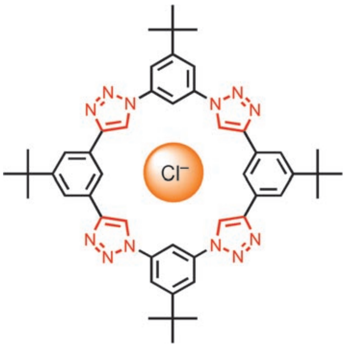
Photosensitized Mass Spectrometry



A TiO_2 photoelectrode array has been designed to achieve efficient photoelectrochemical redox reactions with electron donors or acceptors during the laser desorption ionization process. By adding hydroquinone to a peptide mixture, the photoelectrochemically generated benzoquinone reacts with the cysteine residues to selectively form tagged cysteine-containing peptides, thus demonstrating that in-source oxidation reactions can be efficiently performed.

Anion Receptors

Strength in numbers: When traditionally weak C—H hydrogen bonds are preorganized in a shape-persistent macrocycle, a strong affinity for chloride ions emerges. This discovery arises from the dual use of click chemistry for efficient macrocyclization and the favorable steric properties of the resulting 1,2,3-triazoles.



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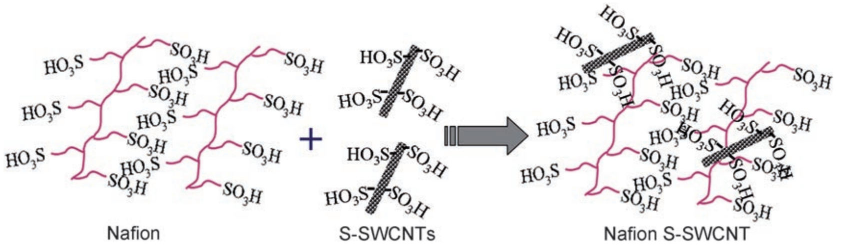
Fuel Cells

R. Kannan, B. A. Kakade,
V. K. Pillai* ______ **2653 – 2656**

Polymer Electrolyte Fuel Cells Using Nafion-Based Composite Membranes with Functionalized Carbon Nanotubes

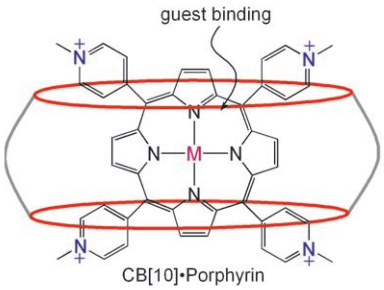


Fuel efficiency: Enhanced proton conductivity is obtained by the incorporation of single-walled carbon nanotubes prefunctionalized with sulfonic acid groups (S-SWCNTs) into a Nafion matrix (see scheme). The acid content of the CNT connects the hydrophobic regions of the membrane, thus providing a network for proton mobility. The polymer electrolyte membranes also have improved mechanical stability in H_2/O_2 fuel cells.

Inclusion Compounds

S. Liu, A. D. Shukla, S. Gadde,
B. D. Wagner,* A. E. Kaifer,
L. Isaacs* ______ **2657 – 2660**

Ternary Complexes Comprising Cucurbit[10]uril, Porphyrins, and Guests

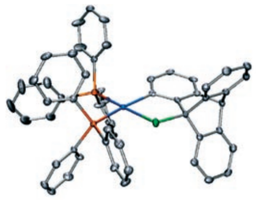


As easy as pi: The spacious 870-Å^3 cavity of CB[10] is able to accommodate free base and metalated tetra(*N*-methylpyridyl)porphyrins inside. The complexes blend the advantageous recognition and photophysical properties of these two classes of macrocycles and promote the formation ternary complexes (see picture) in water through π–π stacking interactions.

Selenium Metallacycles

A. Ishii,* N. Nakata, R. Uchiumi,
K. Murakami ______ **2661 – 2664**

Reactions of a Ditriptycyl-Substituted Selenoseleninate and Related Compounds with a Platinum(0) Complex: Formation of Selenaplatinacycle and Hydrido Selenolato Platinum(II) Complexes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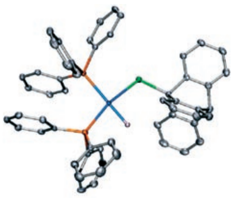
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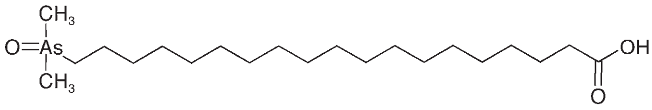
A selenaplatinacycle (see structure **1**; red P, blue Pt, green Se) is formed by the reactions of TripSe(O)SeTrip (Trip = 9-triptycyl) and TripSeOH with $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ by intramolecular C–H activation leading to the cyclometalation. The reaction of TripSeSeTrip with $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ also provided **1** together with TripSeH, which reacts with $[Pt(PPh_3)_2(\eta^2\text{-}C_2H_4)]$ to give the hydrido selenolato platinum(II) complex **2**.

Arsenolipids

A. Rumpler, J. S. Edmonds, M. Katsu,
K. B. Jensen, W. Goessler, G. Raber,
H. Gunnlaugsdottir,
K. A. Francesconi* ______ **2665 – 2667**

Arsenic-Containing Long-Chain Fatty Acids in Cod-Liver Oil: A Result of Biosynthetic Infidelity?

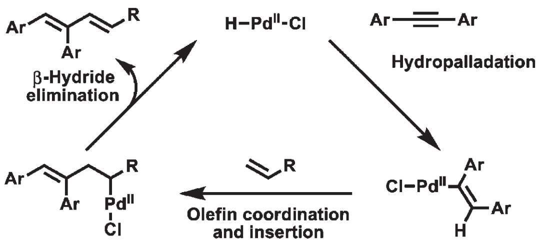


A bit fishy: Six arsenolipids have been isolated from cod-liver oil and identified by HPLC and mass spectrometry as a series of arsenic-containing long-chain fatty acids (for example, see picture). These fatty acids account for about 20% of the total arsenolipid content of cod-liver oil.

Heck Coupling

A. T. Lindhardt (neé Hansen),
M. L. H. Mantel,
T. Skrydstrup* ———— **2668–2672**

Palladium-Catalyzed Intermolecular Ene–Yne Coupling: Development of an Atom-Efficient Mizoroki–Heck-Type Reaction

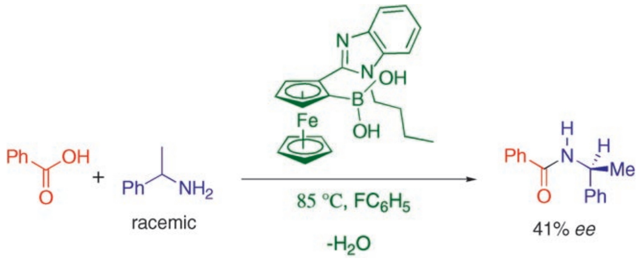


Direct and to the point: A palladium(II) catalytic system based on a palladium hydride species provides access to highly substituted 1,3-dienes through a direct coupling of alkynes with alkenes in a base-free Mizoroki–Heck-type reaction with full atom economy (see scheme; R = amide, borate, C(OH)Me$_2$, O–alkyl).

Amidation

K. Arnold, B. Davies, D. Hérault,
A. Whiting* ———— **2673–2676**

Asymmetric Direct Amide Synthesis by Kinetic Amine Resolution: A Chiral Bifunctional Aminoboronic Acid Catalyzed Reaction between a Racemic Amine and an Achiral Carboxylic Acid



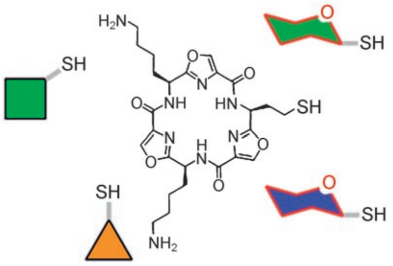
Let's resolve this: A planar chiral benzimidazole ferroceneboronic acid catalyst demonstrates low to moderate asymmetric induction in the kinetic resolution of racemic α-substituted benzylamines by direct amide formation with achiral carboxylic acids (see scheme).

Dynamic Combinatorial Chemistry

A. Bugaut, K. Jantos, J.-L. Wietor,
R. Rodriguez, J. K. M. Sanders,
S. Balasubramanian* ———— **2677–2680**

Exploring the Differential Recognition of DNA G-Quadruplex Targets by Small Molecules Using Dynamic Combinatorial Chemistry

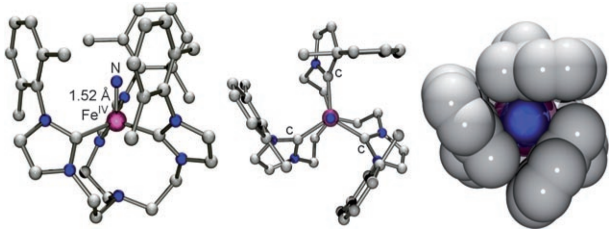
Tuning affinities: Dynamic combinatorial chemistry has been employed to explore the effect of chemical modifications on the DNA G-quadruplex binding properties of an oxazole-based peptide macrocycle. Two dynamic libraries of molecules, containing cationic and carbohydrate motifs, respectively, were screened by using structurally diverse nucleic acid targets (see scheme; each colored shape represents a cation or carbohydrate).



Coordination Chemistry

C. Vogel, F. W. Heinemann, J. Sutter,
C. Anthon, K. Meyer* ———— **2681–2684**

An Iron Nitride Complex



High on nitride: Discrete iron nitride complexes stabilized by N-anchored tris(carbene) ligands have been synthesized (see picture). These high-valent $\mathrm{Fe^{IV}{\equiv}N}$ complexes are stable at room temperature, which allows their full spectroscopic and—for the first time—crystallographic characterization.

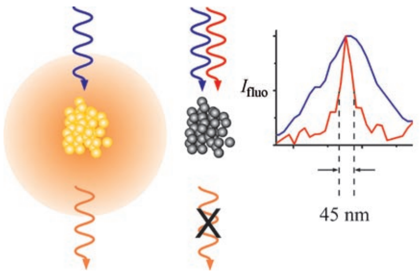
Contents

Nanomaterials

S. E. Irvine, T. Staudt, E. Rittweger,
J. Engelhardt, S. W. Hell* ___ **2685 – 2688**

Direct Light-Driven Modulation of Luminescence from Mn-Doped ZnSe Quantum Dots

Unlimited possibilities: Light-driven modulation of the fluorescence from Mn-doped ZnSe quantum nanocrystals has been established through excited-state absorption and its direct competition with spontaneous emission. Such optical control over electronic transitions enables far-field fluorescence microscopy analysis with diffraction-unlimited resolution (45 nm, red) based on quantum dots (confocal imaging has a resolution of 200 nm, blue).

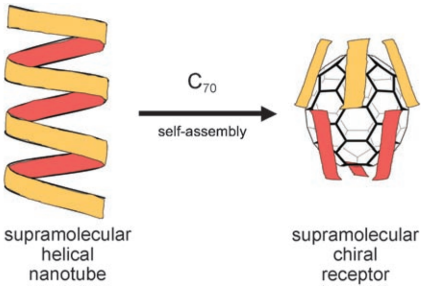


Fullerenes

J.-L. Wietor, G. D. Pantoş,
J. K. M. Sanders* ___ **2689 – 2692**

Templated Amplification of an Unexpected Receptor for C_{70}

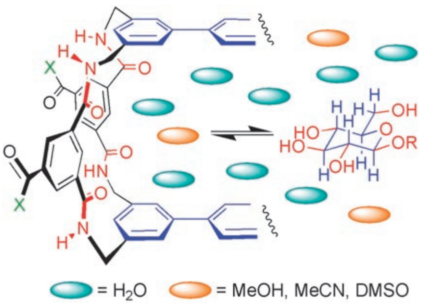
C_{70} mixes things up: C_{70} fullerene triggers the formation of a supramolecular receptor based on amino acid functionalized naphthalene diimides. This hexameric receptor is formed at the expense of a supramolecular helical nanotube (see picture) and highlights the dynamic combinatorial nature of hydrogen-bonded scaffolds.



Carbohydrate Recognition

E. Klein, Y. Ferrand, N. P. Barwell,
A. P. Davis* ___ **2693 – 2696**

Solvent Effects in Carbohydrate Binding by Synthetic Receptors: Implications for the Role of Water in Natural Carbohydrate Recognition

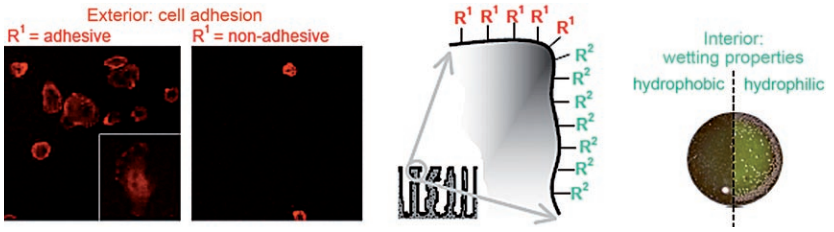


How do they do it? Carbohydrates are intrinsically difficult to bind in water. Lectins and other proteins succeed, but do they use polar or hydrophobic interactions? Studies of synthetic lectins in mixed solvent systems shed new light onto this contentious issue (see scheme; X = hydrophobic or hydrophilic solubilizing groups; R = H or alkyl group).

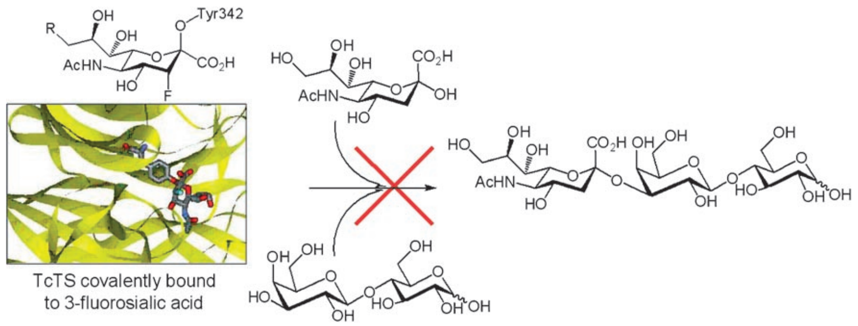
Surface Chemistry

K. A. Kilian, T. Böcking, K. Gaus,
J. J. Gooding* ___ **2697 – 2699**

Introducing Distinctly Different Chemical Functionalities onto the Internal and External Surfaces of Mesoporous Materials



The ins and outs of it: The external and internal surfaces of mesoporous materials can be modified independently by exploiting the wetting behavior of the pores modified with a hydrophobic activated monolayer. To demonstrate the principle, porous silicon photonic crystals were modified with ligands promoting cell adhesion on the top of the crystal and with different functionalities on the inside of the crystal.



A substitution for inhibition: The incorporation of an aryl substituent at C9 of 3-fluorosialyl fluorides provides specificity and dramatically slows the reactivation of the glycosylphosphatidylinositol-anchored surface protein *Trypanosoma cruzi trans*-sialidase (TcTS) by transglycosylation (see picture). X-ray crystallographic analysis of the trapped intermediate has provided a structural rationale for this behavior.

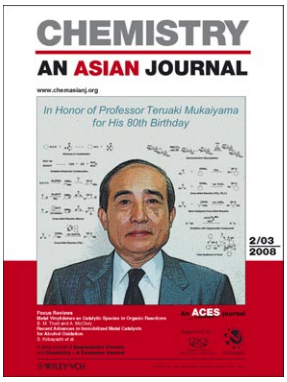
Enzyme Inhibitors

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

For more Information see:



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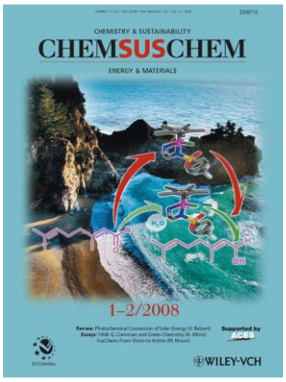

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