Contents

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:

I. Paterson, E. A. Anderson, S. M. Dalby, J. Ho Lim, J. Genovino, P. Maltas, C. Moessner*
Total Synthesis of Spirastrellolide A Methyl Ester. Part 1: Synthesis of an Advanced C17–C40 Bis(spiroacetal) Subunit

*X. Ning, J. Guo, M. A. Wolfert, G.-J. Boons**
Visualizing Metabolically Labeled Glycoconjugates of Living Cells by Copper-Free and Fast Huisgen Cycloadditions

S. Ghosh, A. Mukherjee, P. J. Sadler, S. Verma**
Periodic Iron Nanomineralization in Human Serum Transferrin Fibrils

M. Murata, Y. Ochi, F. Tanabe, K. Komatsu, Y. Murata**
Internal Magnetic Fields of Dianions of Fullerene and Its Cage-Opened Derivatives Studied with Encapsulated H_2 as an NMR Spectroscopic Probe

S. A. Joyce, A. O. Brachmann, I. Glazer, L. Lango, G. Schwär, D. J. Clarke, H. B. Bode**
Bacterial Biosynthesis of a Multipotent Stilbene

*M. Schulz-Dobrick, M. Jansen**
Intercluster Compounds Consisting of Gold Clusters and Fullerides: $[Au_7(PPh_3)_7]C_{60}\cdot THF$ and $[Au_8(PPh_3)_8](C_{60})_2$

Books

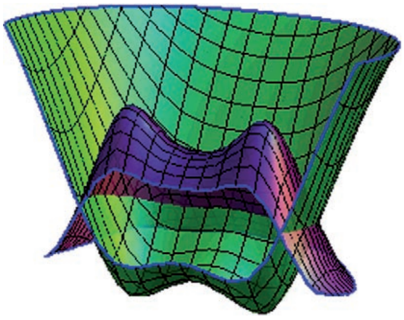
Highlights

Structure of Water

G. Niedner-Schatteburg* —— **1008 – 1011**

Infrared Spectroscopy and Ab Initio Theory of Isolated $H_5O_2^+$: From Buckets of Water to the Schrödinger Equation and Back

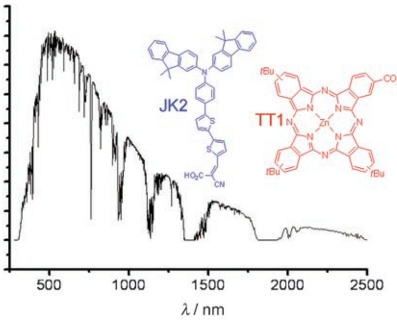
Symmetric and asymmetric at a time: The infrared spectrum of the $H_5O_2^+$ ion, which was only attained a few years ago by demanding supersonic jet expansion experiments, can now be simulated with elaborate theoretical methods. Naked $H_5O_2^+$ transfers a proton exactly as predicted for fully hydrated $H_5O_2^+$. A gap in the description of proton diffusion in water which was begun over 200 years ago has thus been closed.



Light Harvesters

N. Robertson* ———— **1012 – 1014**

Catching the Rainbow: Light Harvesting in Dye-Sensitized Solar Cells



Brand new combined harvesters: The development of low-cost dyes for photovoltaic systems which harvest solar radiation (spectrum shown) over a broad spectral range has proven difficult. Cosensitization using more than one dye (for example JK2 and TT1 in picture) is an emerging method to extend the spectral coverage, and may lead to higher energy-conversion efficiencies.

Contents

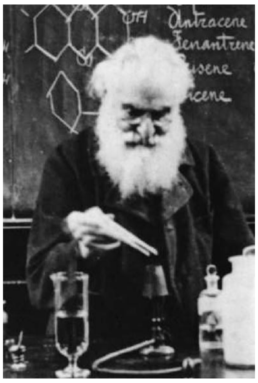
Essays

History of Chemistry

T. T. Tidwell* ——— **1016 – 1020**

Hugo (Ugo) Schiff, Schiff Bases, and a Century of β-Lactam Synthesis

Schiff—the man and the base: Hugo Schiff (1834–1915) studied with Friedrich Wöhler in Germany, but because of his liberal views spent almost his entire career in Italy, where he prepared and characterized Schiff bases (imines) and made many other chemical investigations. His scientific career spanned more than 60 years, and he lived to see the utilization of Schiff bases in [2+2] cycloadditions with ketenes to form β-lactams.

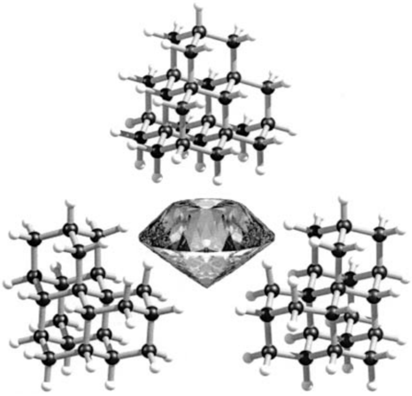


Reviews

Diamondoid Chemistry

H. Schwertfeger, A. A. Fokin,*
P. R. Schreiner* ——— **1022 – 1036**

Diamonds are a Chemist's Best Friend: Diamondoid Chemistry Beyond Adamantane



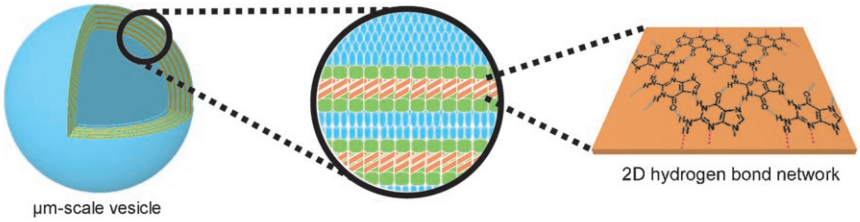
Diamondoids are forever: The increasing availability of diamondoids in large amounts from crude oil opens the door to a virtually unstudied class of carbon-rich materials. These diamond nanostructures not only have well-defined structures but also represent the most stable form of hydrocarbons on the nanometer scale. Their functionalization and characterization has resulted in compounds that are ready for testing as pharmaceuticals, coatings, polymers, molecular junctions, and electronic devices.

Communications

Supramolecular Chemistry

I. Yoshikawa, J. Sawayama,
K. Araki* ——— **1038 – 1041**

Highly Stable Giant Supramolecular Vesicles Composed of 2D Hydrogen-Bonded Sheet Structures of Guanosine Derivatives



Stabilized net: A molecular design approach to protect a 2D hydrogen-bonding network with nonpolar shielding layers has allowed the fabrication of micrometer-scale supramolecular vesicles in water (see picture). These hydrogen-bond-directed giant vesicles and their dispersions in aqueous media show high stability under various conditions.

For the USA and Canada:
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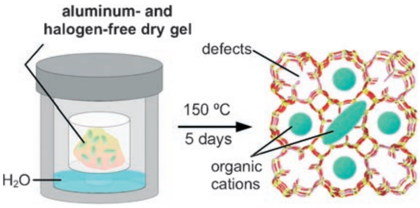
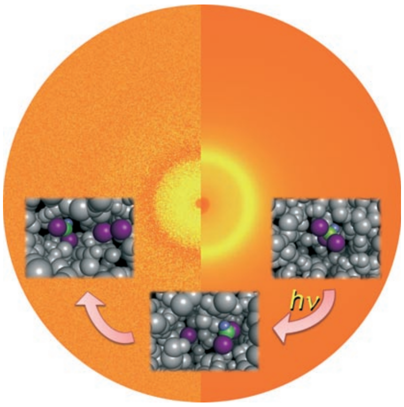


Hot and steamy cages: The gel composition for MCM-68 typically obtained by hydrothermal methods is changed by steam-assisted crystallization and results in the formation of the highly crystalline pure silica analogue YNU-2P (see picture). The crystal structure of this compound indicates the presence of significant site defects.

Microporous Silicates

Y. Koyama, T. Ikeda, T. Tatsumi,
Y. Kubota* ——— **1042 – 1046**

A Multi-Dimensional Microporous Silicate That Is Isomorphous to Zeolite MCM-68



The structural dynamics of the photodissociation of iodoform in methanol (see picture: H blue, C green, I violet) are revealed by means of time-resolved X-ray diffraction in solution (also called transient X-ray liquidography because of its analogy to crystallography). While spectroscopic studies suggest the existence of isoiodoform, no signals are observed for this intermediate species in time-resolved diffraction experiments performed using time delays between 100 ps and 3 μs.

Time-Resolved Studies

J. H. Lee, J. Kim, M. Cammarata, Q. Kong,
K. H. Kim, J. Choi, T. K. Kim, M. Wulff,
H. Ihee* ——— **1047 – 1050**

Transient X-ray Diffraction Reveals Global and Major Reaction Pathways for the Photolysis of Iodoform in Solution

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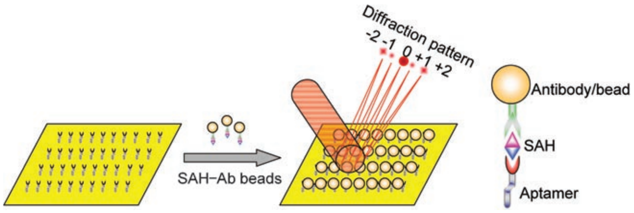

I saw the SAH: Clinically relevant concentrations of *S*-adenosyl homocysteine (SAH) can be rapidly detected using self-assembled diffraction gratings. SAH bound to antibody-conjugated (Ab) microbeads (see picture) and then incubated with a gold chip functionalized with SAH-specific aptamer in alternating line patterns produces gratings that are detected by optical diffraction intensity measurements (detection limit: 64 pmol L^{-1}).

Diffraction Gratings

G. Acharya, C.-L. Chang, D. P. Holland,
D. H. Thompson,*
C. A. Savran* ——— **1051 – 1053**

Rapid Detection of *S*-Adenosyl Homocysteine Using Self-Assembled Optical Diffraction Gratings

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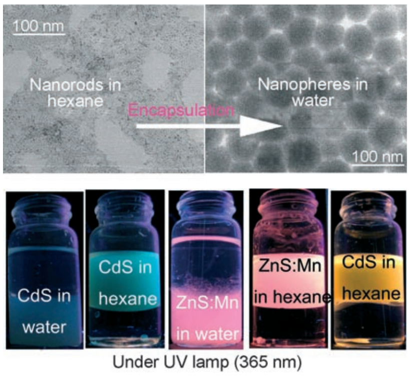


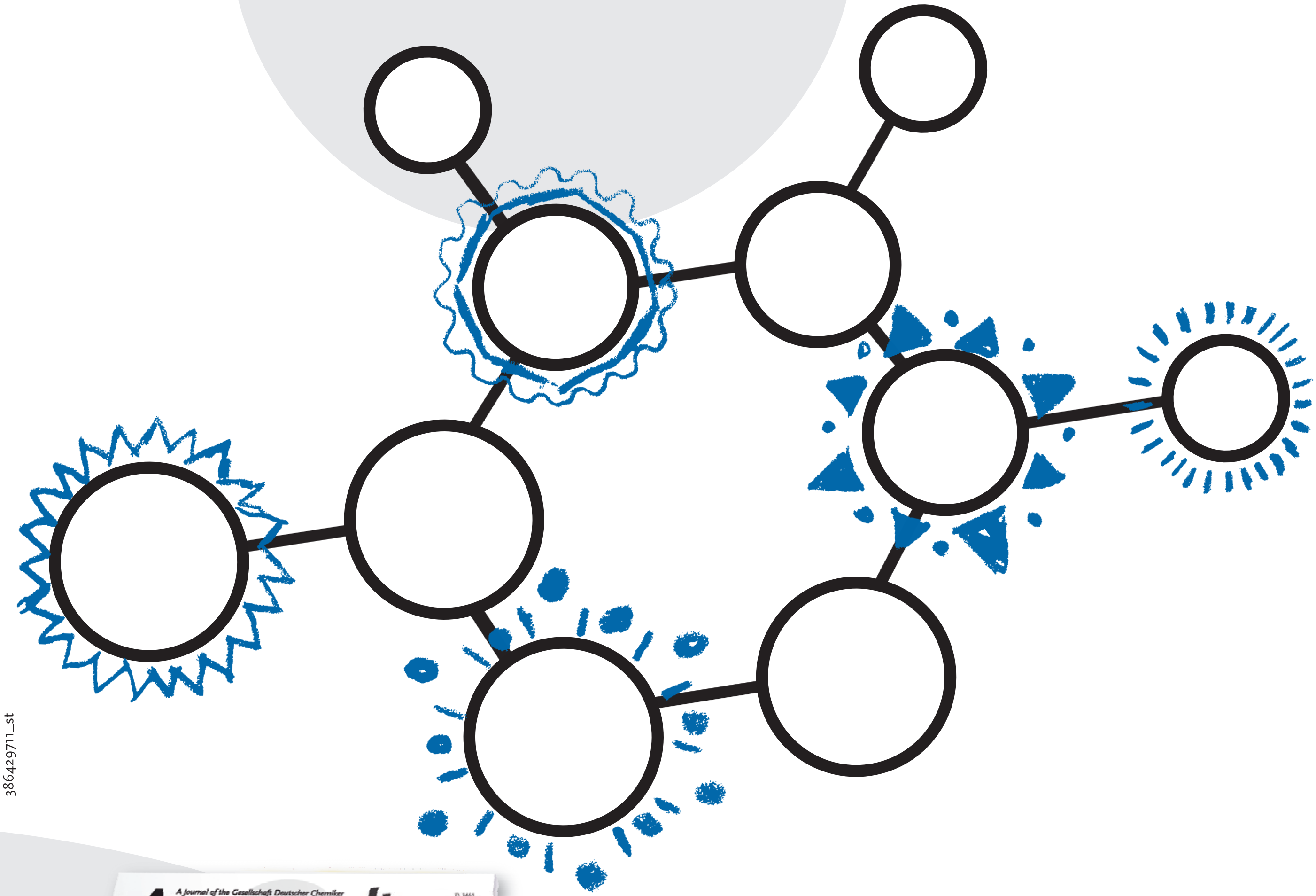
A cure for hydrophobia: Monodisperse semiconductor nanorods are synthesized using nitrates as precursors. The surface modification of these hydrophobic nanocrystals is accomplished through encapsulation with a carboxylic acid enriched polymer (see TEM images), which leads to hydrophilic, bioconjugatable nanospheres for use in multicolor biolabeling applications.

Nanostructures for Biolabeling

L. Y. Wang, P. Li, J. Zhuang, F. Bai, J. Feng,
X. Y. Yan, Y. D. Li* ——— **1054 – 1057**

Carboxylic Acid Enriched Nanospheres of Semiconductor Nanorods for Cell Imaging

Incredibly versatile!



A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org
2007–46/9
1st March Issue
Magnetic Materials
Total Synthesis of Quinine
J. I. Seeman
Thermally Responsive Polymer Vesicles
Y. Morishima
Decarboxylative Biaryl Coupling
O. Baudoin
WILEY-VCH

Theme variety on the one hand: Many articles in *Angewandte Chemie* cover the classical themes such as organic synthesis or coordination chemistry. Besides these, current topics like (bio)nanotechnology, chemical biology, and green chemistry are well represented. And then there are the „must-see articles“, such as those on the detection of anthrax spores*, or the characteristic scent of iron,** or the artificial lily-of-the-valley flavor.***
Section variety on the other: Communications, Reviews, Highlights, Essays, Obituaries, Meeting Reviews, as well as Website and Book Reviews are regularly found in *Angewandte*.

* M. Tamborrini, D.B. Werz, J. Frey, G. Pluschke, P.H. Seeberger, Angew. Chem. Int. Ed. 2006, 45, 6581-6582.
** D. Glindemann, A. Dietrich, H.-J. Staerk, P. Kuschk, Angew. Chem. Int. Ed. 2006, 45, 7006 - 7009.
*** L. Doszczak, P. Kraft, H.-P. Weber, R. Bertermann, A. Triller, H. Hatt, R. Tacke, Angew. Chem. Int. Ed. 2007, 46, 3367--3371

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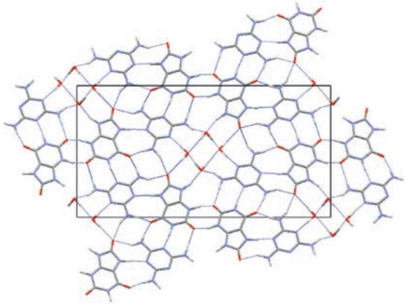
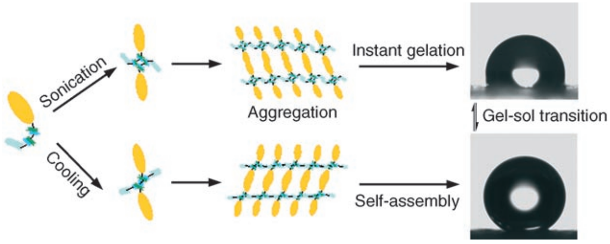
WILEY-VCH

38642971_st

Making plans for hydrogels: Calculations successfully predict the molecular structure of a robust hydrogel. Melamine and uric acid cocrystallize with water upon sonication, and using experimental data, the minimized structure (see picture) was calculated and successfully compared with powder X-ray diffraction data of the xerogel.

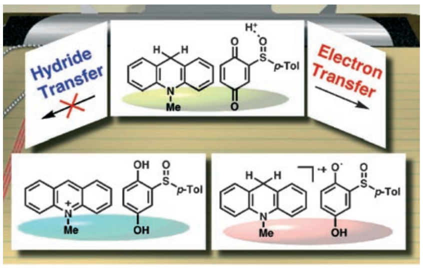


Hydrogelation



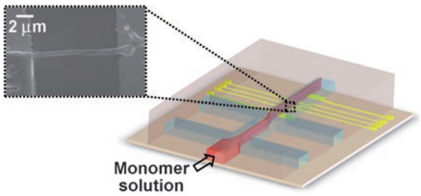
Sound effects: The morphologies and surface properties of a cholesterol-based assembly with two hydrogen-bond sites per molecule can be controlled by ultrasound stimuli and restored by a thermal process. The cooperation competition of intra- and intermolecular hydrogen bonds and hydrophobic interactions, regulated by sonication or thermal processes, are suggested to be the main contributions toward the self-assembly (see schematic of gelation process and wettability tests).

Organogels



An electron-transfer pathway is preferred to a direct hydride-transfer pathway in two-electron reduction of protonated 1-(*p*-tolylsulfinyl)-2,5-benzoquinone by the NADH analogue 10-methyl-9,10-dihydroacridine, as has been demonstrated for the first time by ESR detection of the resulting radical cation of the acridine derivative (see picture).

NADH Model Reaction



Working patterns: Size-controllable electrochemical deposition of conducting polymer micropatterns across individually addressable electrode junction pairs (inset) is achieved with a hydrodynamically focused laminar stream in a microfluidic setting (see picture). Such a focused stream can be used as a dynamic template for sequential production of sensor arrays capable of detecting extremely small quantities of analytes.

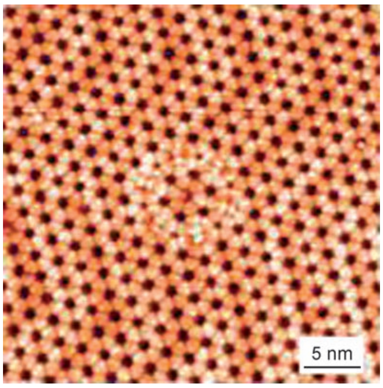
Polymer Micropatterning

Self-Assembly on Surfaces

M. Pivetta,* M.-C. Blüm, F. Patthey, W.-D. Schneider ______ **1076 – 1079**

Two-Dimensional Tiling by Rubrene Molecules Self-Assembled in Supramolecular Pentagons, Hexagons, and Heptagons on a Au(111) Surface

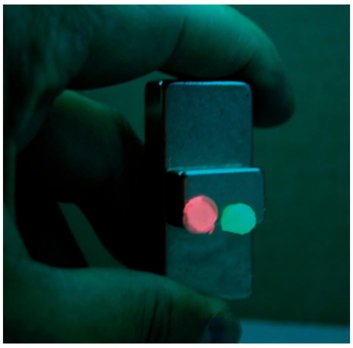
Tiling patterns: Rubrene ($C_{42}H_{28}$) molecules self-assemble on a gold surface to create a two-dimensional tiling with a combination of slightly distorted supramolecular pentagons, hexagons, and heptagons. Both periodic and nonperiodic tessellations are observed, as well as circular singularities in extended honeycomb domains, formed by the replacement of a ring of twelve hexagons by six pentagon-heptagon pairs.



Metal–Organic Frameworks

B. V. Harbuzaru, A. Corma,* F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos, J. Rocha* ______ **1080 – 1083**

Metal–Organic Nanoporous Structures with Anisotropic Photoluminescence and Magnetic Properties and Their Use as Sensors



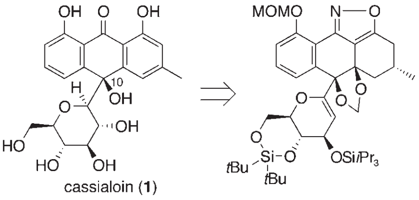
Shining bright: Porous metal–organic framework materials are important owing to their potential applications as sensors. A new family of nanoporous, multifunctional rare-earth metal–organic materials displays emission quantum yields and efficiencies that are the highest reported for solid-state Eu^{3+} compounds with organic ligands and magnetic properties. The picture shows [Gd,Eu]- and [Tb]-containing materials under UV light and interacting with a magnet.

Natural Product Synthesis

Y. Koyama, R. Yamaguchi, K. Suzuki* ______ **1084 – 1087**

Total Synthesis and Structure Assignment of the Anthrone C-Glycoside Cassialoin

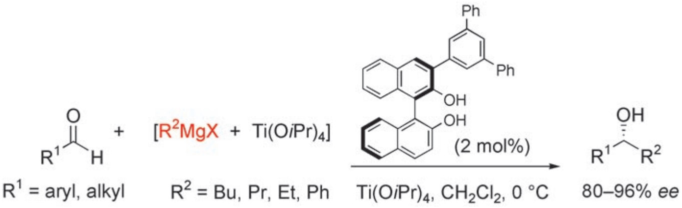
Configuration confirmed: The first total synthesis and structure assignment of the anthrone C-glycoside cassialoin (**1**) have been achieved by exploiting an isoxazole-containing stereogenic α-ketol and a subsequent intramolecular redox reaction (see retrosynthetic analysis; MOM = methoxymethyl).



Asymmetric Catalysis

Y. Muramatsu, T. Harada* ______ **1088 – 1090**

Catalytic Asymmetric Alkylation of Aldehydes with Grignard Reagents

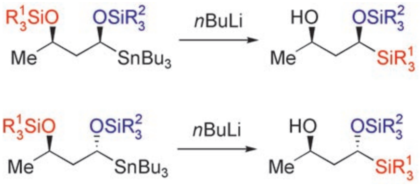


Added benefits: Grignard reagents can be employed in the asymmetric alkylation of aldehydes by using a titanium(IV) catalyst derived from binol in the presence of excess titanium tetraisopropoxide (see scheme). The reaction proceeds with a low catalyst loading (2 mol%) and exhibits high enantioselectivity for both aromatic and unsaturated aldehydes and for both alkyl and aryl Grignard reagents.

Asymmetric Rearrangements

Y. Mori,* Y. Futamura,
K. Horisaki ———— 1091 – 1093

Regioselective Aliphatic Retro-[1,4]-Brook Rearrangements

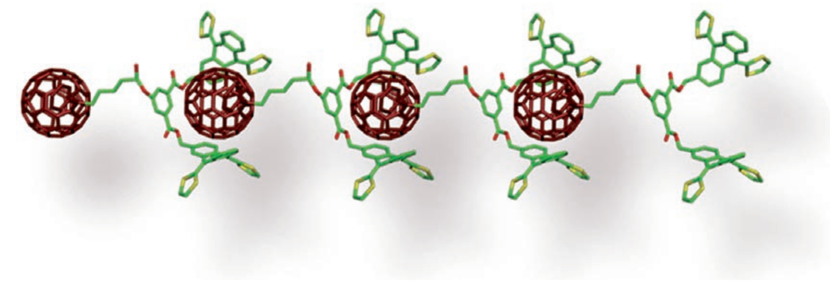


A turn-up for the Brook: The relative ease of silyl migration in the aliphatic retro-Brook rearrangements of α,γ-disilyloxy organolithium compounds (see scheme) has been revealed for the first time to be $[1,2] \ll [1,4]$. The increasing size of the silyloxy group at the γ position relative to that at the α position induces higher [1,4] selectivity.

Supramolecular Polymers

G. Fernández, E. M. Pérez, L. Sánchez,
N. Martín* ———— 1094 – 1097

Self-Organization of Electroactive Materials: A Head-to-Tail Donor–Acceptor Supramolecular Polymer

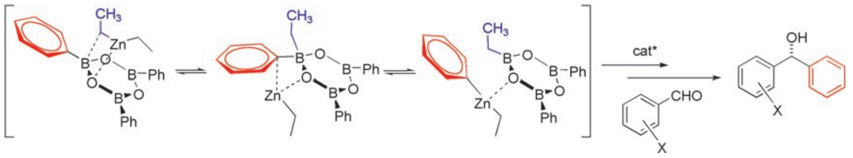


Fullerenes do the conga! Synthesis and self-recognition of a monomer featuring a specially designed receptor for [60]fullerene are described. The monomer self-assembles in a head-to-tail fashion through π–π interactions, thus forming a linear oligomeric species in solution (see image). The formation of this redox-amphoteric supramolecular polymer represents a new approach to the controlled organization of electroactive materials.

Asymmetric Catalysis

C. Jimeno, S. Sayalero, T. Fjermestad,
G. Colet, F. Maseras,*
M. A. Pericàs* ———— 1098 – 1101

Practical Implications of Boron-to-Zinc Transmetalation for the Catalytic Asymmetric Arylation of Aldehydes

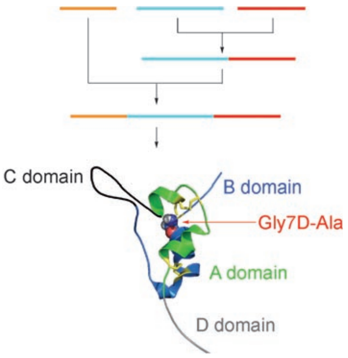


Faster than believed: Transmetalation from aryl boronic acids and triaryl boroxines to diethylzinc takes place within minutes following a two-step, low-energy pathway (see picture), according to density functional calculations and reaction microcalorimetry measurements. The experimental conditions for a practical, atom-economical, and highly enantioselective catalytic arylation of a variety of aldehydes have been developed from these data.

Chemical Protein Synthesis

Y. Sohma, B. L. Pentelute, J. Whittaker,
Q.-X. Hua, L. J. Whittaker, M. A. Weiss,
S. B. H. Kent* ———— 1102 – 1106

Comparative Properties of Insulin-like Growth Factor 1 (IGF-1) and [Gly7D-Ala]IGF-1 Prepared by Total Chemical Synthesis



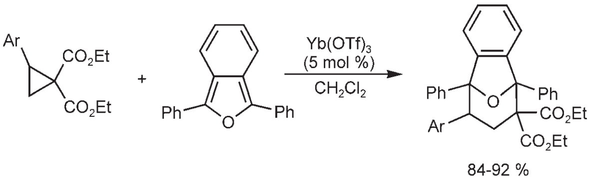
Chemistry for biology: IGF-1 and [Gly7D-Ala]IGF-1 have been prepared by a total chemical synthesis and their folding and receptor-binding properties compared (see scheme). This approach facilitates the introduction of nonstandard amino acids whose biosynthetic incorporation is difficult or not feasible and thus promises to lead to a new generation of structure–activity studies of potential interest in the treatment of cancer and diabetes mellitus.

Contents

Cycloaddition

O. A. Ivanova,* E. M. Budynina,
Y. K. Grishin, I. V. Trushkov,
P. V. Verteletskii ______ **1107 – 1110**

Donor–Acceptor Cyclopropanes as Three-Carbon Components in a [4+3] Cycloaddition Reaction with 1,3-Diphenylisobenzofuran

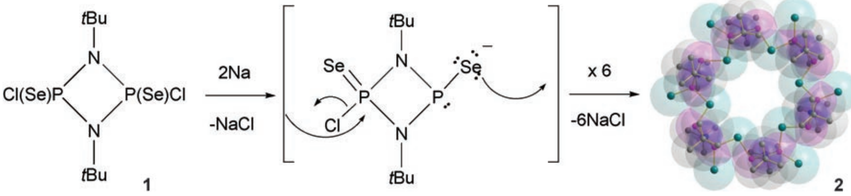


Dienophiles with a difference: 2-Aryl 1,1-bis(alkoxycarbonyl) cyclopropanes undergo the title reaction under the catalysis of ytterbium triflate ($Yb(OTf)_3$) in excellent yield (see scheme). Under mild reaction conditions, the major product is the less stable *exo* isomer. At higher temperatures, the *endo* isomer is obtained exclusively, as the *exo* cycloadduct decomposes through cycloreversion.

Inorganic Macrocycles

S. González-Calera, D. J. Eisler, J. V. Morey,
M. McPartlin, S. Singh,*
D. S. Wright* ______ **1111 – 1114**

The Selenium-Based Hexameric Macrocycle $[(Se{=})P(\mu\text{-N}t\text{Bu})_2P(\mu\text{-Se})]_6$

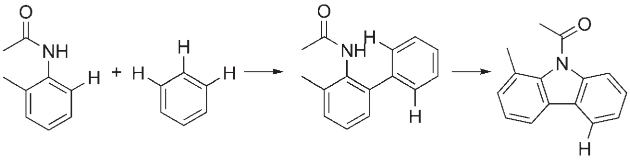


Head-to-Tail: The Wurtz reaction of the dimer $[(Cl)(Se{=})P(\mu\text{-N}t\text{Bu})]_2$ (**1**) with sodium metal gives the inorganic macrocycle $[(Se{=})P(\mu\text{-N}t\text{Bu})_2P(\mu\text{-Se})]_6$ (**2**), arising from cyclization of a selenium-centered nucleophilic intermediate. The inorganic macrocyclic backbone contains alternating P^{III} and P^{V} centers and possesses an 8.2-Å-diameter cavity.

C–H Activation

B.-J. Li, S.-L. Tian, Z. Fang,
Z.-J. Shi* ______ **1115 – 1118**

Multiple C–H Activations To Construct Biologically Active Molecules in a Process Completely Free of Organohalogen and Organometallic Components

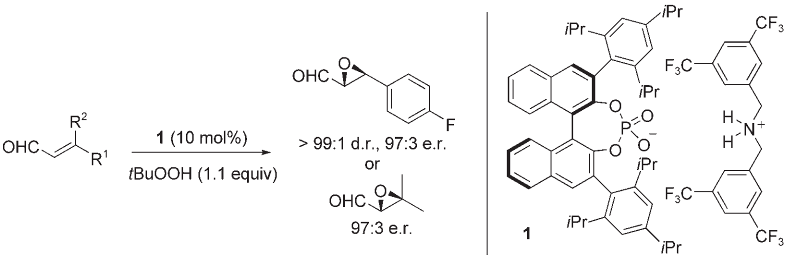


Step by step: Highly selective cross dehydrogenative arylation of acetanilides was developed to construct biaryls under mild condition. With this method, different aryl C–H bonds were activated in sequential reactions to construct functionalized carbazoles (see scheme), which are present as key structural units in various biological molecules and organic optical materials.

Asymmetric Catalysis

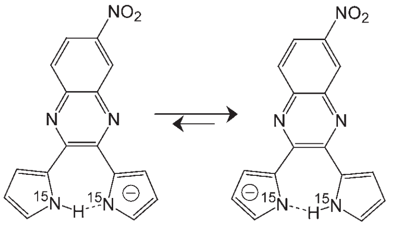
X. Wang, B. List* ______ **1119 – 1122**

Asymmetric Counteranion-Directed Catalysis for the Epoxidation of Enals



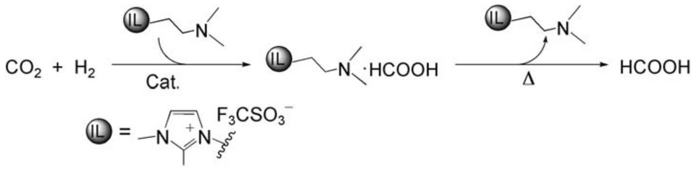
A new mode of chiral anion catalysis: A powerful chiral-counteranion strategy for catalytic asymmetric epoxidations using the newly discovered catalyst **1** has been applied to the epoxidation of α,β-unsaturated aldehydes together with *tert*-butyl hydroperoxide as the oxidant (see scheme). Remarkably, this system provides the corresponding epoxides in high diastereo- and enantioselectivity for both di- and trisubstituted enals.

Hydrogen Bonds



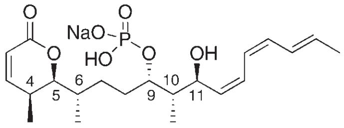
Tug of war: Treatment of the doubly ^{15}N-labeled anion receptor 6-nitro-2,3-dipyrrol-2-ylquinoxaline with solid sodium hydride in CD_2Cl_2/[D$_6$]DMSO leads to the monodeprotonated anion (see picture). The NMR data indicate the formation of a very strong intramolecular NHN hydrogen bond, with a scalar ^{15}N–^{15}N coupling constant of 16.5 Hz, the largest value observed to date.

Catalytic Hydrogenation



A basic hydrogenation catalyst: The combination of a basic ionic liquid (IL) and a supported ruthenium complex catalyzes the hydrogenation of CO_2 with satisfactory activity and selectivity (see scheme). The resulting formic acid is easily collected and the ionic liquid and catalyst can be reused directly after an easy separation step.

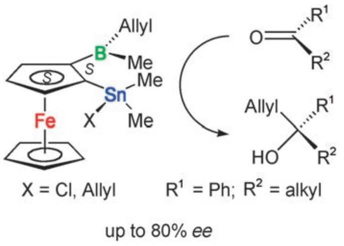
Natural Products



cytostatin
(4*S*,5*S*,6*S*,9*S*,10*S*,11*S*)

Mix and match: Four closely related candidate isomers for cytostatin have been synthesized by using the technique of fluorous mixture synthesis. Comparison of NMR, thin-layer chromatography, and optical rotation data enabled the three isomers that were not cytostatin to be identified. Thus, by a process of elimination (disproof), the isomer corresponding to cytostatin was determined, and the 4*S*,5*S*,6*S*,9*S*,10*S*,11*S* configuration confirmed.

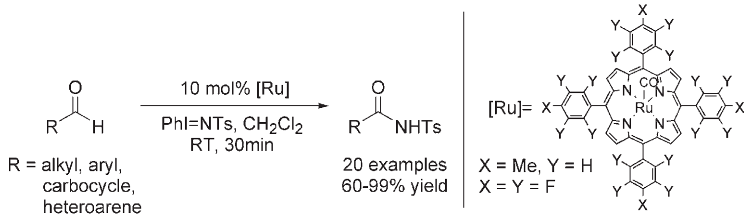
Chiral Lewis Acids



Flat, like your hand: The heteronuclear bidentate Lewis acid 1,2-Fc(BMeCl)(SnMe$_2$Cl) is readily resolved into its constituent enantiomers through highly stereoselective complexation with *N*-methylpseudoephedrine. The resulting planar chiral Lewis acids show optical purities greater than 97% and, upon conversion to the respective allylborane derivatives (see scheme), rapidly add to ketones with enantiomeric excess of up to 80%.

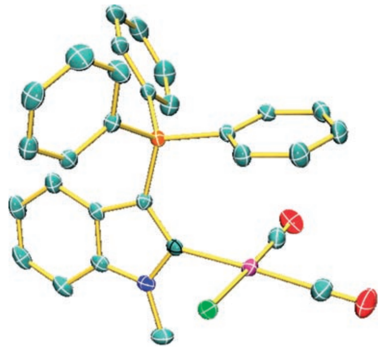
Contents

Amide Bond Formation



H to N: The first example of a mild, highly efficient C–H bond amidation catalyzed by ruthenium(II) porphyrin complexes uses PhI=NTs as the nitrogen source for installing the amide bond functionality in a wide variety of aldehydes (see scheme). The protocol is chemoselective, with the new C–N bond forming only at the acyl C–H bond, even in aldehyde substrates containing other functional groups.

Carbenes



A generous giver: Rh and Pd complexes of an ylide-substituted carbene were synthesized. The carbonyl stretching vibration of the Rh complex (see picture; Rh purple, C turquoise, N blue, O red, P orange, Cl green) was observed at the lowest wavenumber of all *cis*-[RhCl(CO)$_2$(carbene)] complexes known to date, which indicates that this is the strongest known electron-donating carbene.

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

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

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