



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:

R. Klajn, A. O. Pinchuk, G. C. Schatz, B. A. Grzybowski* Synthesis of Heterodimeric Sphere-Prism Nanostructures through Metastable Gold Supraspheres

S. J. George, Z. Tomovic, M. M. J. Smulders, T. F. A. de Greef, P. E. L. G. Leclère, E. W. Meijer, * A. P. H. J. Schenning* Helicity Induction and Amplification in an Oligo(p-phenylenevinylene) Assembly through Hydrogen-Bonded Chiral Acids

M. Kögl, L. Brecker, R. Warrass, J. Mulzer* Total Synthesis and Configurational Assignment of Pasteurestin A and B

J. Wang, X. Hu, J. Jiang, S. Gou, X. Huang, X. Liu, X. Feng* Asymmetric Activation of tropos 2,2'-Biphenol with Cinchonine Generating a Remarkably Effective Catalyst for the Asymmetric Strecker Reaction of N-Tosyl-Protected Aldimines and Ketoimines

A. J. Vegas, J. E. Bradner, W. Tang, O. M. McPherson, E. F. Greenberg, A. N. Koehler, S. L. Schreiber*

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

H. Chen, S. Yang, A. Wortmann, R. Zenobi*

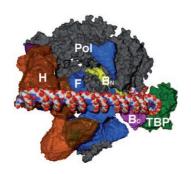
Neutral Desorption Sampling of Living Objects for Rapid Analyses by Extractive Electrospray Ionization Mass Spectrometry

Books

Biocatalysis in the Pharmaceutical and Biotechnological Industries

Ramesh N. Patel

reviewed by A. S. Bommarius _____ 6953



Life under the microscope: Transcription, the copying of a DNA strand to produce an RNA strand, is a central operation in biology. The complex mechanism of eukaryotic transcription has been broken down into molecular details through the work of Roger Kornberg. The Nobel Prize winner for Chemistry describes here first hand the course of his research. The picture shows the pre-initiation complex that must be formed for initiation of transcription.

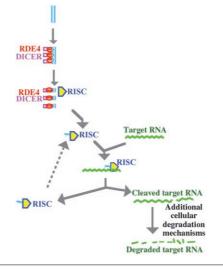
Reviews

Mechanism of Gene Transcription

R. Kornberg* __ **—** 6956 – 6965

The Molecular Basis of Eukaryotic Transcription (Nobel Lecture)

Shhh! Gene silencing is a cell process in which the action of double-stranded RNA molecules suppresses the expression of single genes. Decisive contributions to this area have been made by Andrew Fire and Craig C. Mello, for which they have been awarded the Nobel Prize for Medicine. The Nobel Laureates describe here first hand their research.



RNA Interference

A. Z. Fire* ___

Gene Silencing by Double-Stranded RNA (Nobel Lecture)

Gene Silencing

C. C. Mello* _ 6985 - 6994

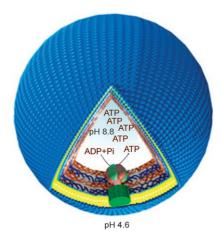
Return to the RNAi World: Rethinking Gene Expression and Evolution (Nobel Lecture)

Communications

Biomimetic Synthesis

L. Duan, Q. He, K. Wang, X. Yan, Y. Cui, H. Möhwald, J. Li* _______ 6996 – 7000

Adenosine Triphosphate Biosynthesis Catalyzed by F_oF₁ ATP Synthase Assembled in Polymer Microcapsules Energy spheres: A biomimetic system consisting of the assembly of F_oF_1 ATPase in lipid-modified polyelectrolyte microcapsules enables adenosine triphosphate (ATP) to be synthesized and stored in the hollow shells, which thereby act as containers for energy storage (see schematic representation; ADP: adenosine diphosphate; Pi: inorganic phosphate).

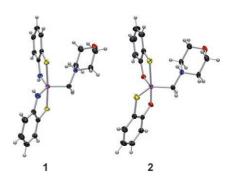


Silicon Complexes

D. Troegel, C. Burschka, S. Riedel, M. Kaupp, R. Tacke* _____ 7001 – 7005

Unusual Silicon Coordination Polyhedra: Non-VSEPR Structures of Zwitterionic λ^5 -Si Silicon(IV) Complexes with an SiS_2N_2C or SiS_2O_2C Skeleton

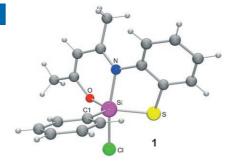
Trading places: The pentavalent silicon compounds 1 and 2 with distorted trigonal-bipyramidal Si coordination polyhedra contain sulfur atoms that occupy axial positions, which contradicts VSEPR predictions for these zwitterionic compounds. These findings are supported by DFT and MP2 calculations (S yellow, Si magenta, O red, N blue, C gray).



Silicon Complexes

S. Metz, C. Burschka, D. Platte, R. Tacke* ______ **7006 – 7009**

Pentacoordination of Silicon by Five Different Ligand Atoms: Neutral Silicon(IV) Complexes with SiCISONC and SiISONC Skeletons

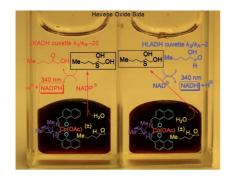


Take five: Pentacoordinate silicon with five different ligand atoms (SiCISONC and SiISONC skeletons) has been realized with the synthesis of the neutral silicon (IV) compound 1 and its iodo analogue, both of which exist in the solid state and in solution. The chloro ligand of 1 can be easily replaced to give further pentacoordinate silicon compounds.

For the USA and Canada:

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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/



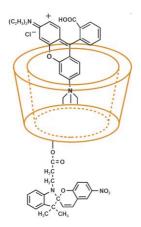
Put the cassette in: An in situ enzymatic screen can give real-time estimates of the sense and magnitude of enantioselectivity across more than one substrate. Screening identified Co^{III} -salen catalysts with β pinene- and α -naphthylalanine-derived chiral scaffolds with broad, yet complementary, substrate specificities.

ADH = alcohol dehydrogenase, HL = horse liver, LK = Lactobacillus kefir, salen = (salicylidene)ethylenediamine.

Combinatorial Chemistry

S. Dey, D. R. Powell, C. Hu, D. B. Berkowitz* ___ 7010 - 7014

"Cassette" In Situ Enzymatic Screening Identifies Complementary Chiral Scaffolds for Hydrolytic Kinetic Resolution Across a Range of Epoxides

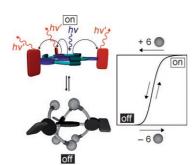


A complex light switch: Photoreversible fluorescence modulation was achieved by supramolecular complexation of a guest rhodamine molecule (RhB) with spiropyran-modified cyclodextrin (see picture). Upon UV irradiation, the chromophore within the cyclodextrin cavity can transfer its energy to the spiropyran moiety, while upon visible-light irradiation, no energy transfer occurs. Thus, light can be used to turn "on" and "off" the fluorescence emission of a dye inside the cyclodextrin cavity.

Fluorescence Modulation

S. Wu,* Y. Luo, F. Zeng, J. Chen, Y. Chen, _____ 7015 **– 70**18 Z. Tong _

Photoreversible Fluorescence Modulation of a Rhodamine Dye by Supramolecular Complexation with Photosensitive Cyclodextrin

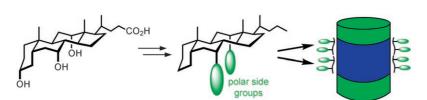


Cooperative structural folding and unfolding of a dynamic multichromophore array provides an unusual signal amplification as part of a resonance energy transfer from the central donor unit to peripheral acceptor ensembles. The stepwise addition and removal of chemical input signals resulted in reversible, sigmoidal response curves in both the turn-on and turn-off scans (see picture).

Allosteric Switches

J. A. Riddle, X. Jiang, J. Huffman, _ 7019 - 7022 D. Lee* _____

Signal-Amplifying Resonance Energy Transfer: A Dynamic Multichromophore Array for Allosteric Switching



An added dimension: Amphiphiles with two-dimensional hydrophobic and hydrophilic faces represent a departure from traditional one-dimensional polar-head/ nonpolar-tail molecules for the stabilization of integral membrane proteins. A

prototypical example of this design has been synthesized from cholic acid (see picture), and was successfully used in the stabilization of two integral membrane proteins (represented by the blue/green cylinder).

Facial Amphiphiles

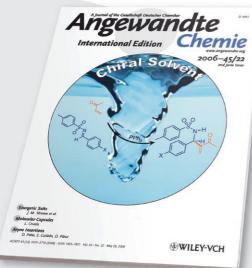
Q. Zhang,* X. Ma, A. Ward, W.-X. Hong, V.-P. Jaakola, R. C. Stevens, M. G. Finn, G. Chang ______ 7023 - 7025

Designing Facial Amphiphiles for the Stabilization of Integral Membrane **Proteins**

6939

Incredibly reader-friendly!





An aesthetically attractive cover picture that arouses curiosity, a well-presented and most informative graphical table of contents, and carefully selected articles that are professionally edited give *Angewandte Chemie* its distinctive character, which allows both easy browsing and further in-depth reading. Nearly 20 well-trained chemists, as well as eight further associates, work week in and week out to assemble reader-friendly issues and daily Early View articles online.



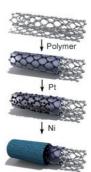


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Full metal jacket: Carbon nanotubes (CNTs) are used as templates to form well-defined anisotropic magnetic nanowires with ferromagnetic behavior at room temperature. Uniform assembly of catalytic Pt nanoparticles on the CNTs yields organic-inorganic hybrid composites that serve as 1D substrates for the preparation of magnetic CNT-supported Ni/NiO nanotubes (see picture).



Magnetic Nanotubes

M. Grzelczak, M. A. Correa-Duarte,*

V. Salgueiriño-Maceira,

B. Rodríguez-González, J. Rivas,

L. M. Liz-Marzán ______ 7026 - 7030

Pt-Catalyzed Formation of Ni Nanoshells on Carbon Nanotubes

Reporting live: A caged β-lactam-D-luciferin (Bluco) conjugate can image β lactamase activity in vivo through a twostep enzymatic process. This novel bioluminogenic probe should facilitate the detection of β -lactamase and widen its applications as a reporter.

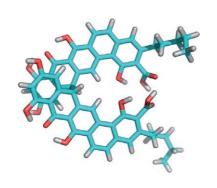


Imaging Probes

H. Yao, M.-K. So, J. Rao* ___ **7031 - 7034**

A Bioluminogenic Substrate for In Vivo Imaging of β-Lactamase Activity

A'gem' of an enzyme: Geminal enzymatic bismethylation in the biosynthetic pathway leading to the cytotoxic polyketide benastatin blocks the highly reactive benzylic position of an anthrone-type intermediate. In a mutant lacking the Cmethyl transferase, quinones and structurally intriguing meso and rac dimers (see calculated structure) are formed, which were elucidated by a combination of spectroscopy and computational simulations.



Biosynthesis

A. Schenk, Z. Xu, C. Pfeiffer, C. Steinbeck, C. Hertweck* _____ 7035 - 7038

Geminal Bismethylation Prevents Polyketide Oxidation and Dimerization in the Benastatin Pathway



"Attractive" catalyst: Molybdenum oxide nanoparticles have been incorporated into a mesoporous silica shell and coated on silica-coated magnetite nanoparticles for use as a magnetically separable hetero-

geneous epoxidation catalyst. This catalyst, which has a low Mo loading of 1 mol%, can be recycled and reused six times in the epoxidation of cis-cyclooctene with no major loss of activity (see picture).

Heterogeneous Catalysis

M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang, T. Hyeon* ______ 7039 - 7043

A Magnetically Recyclable Nanocomposite Catalyst for Olefin **Epoxidation**

6941

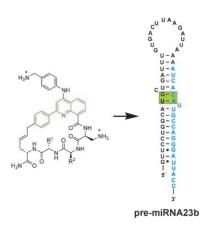
Contents

RNA Recognition

M. Krishnamurthy, K. Simon,
A. M. Orendt, P. A. Beal* ____ 7044-7047

Macrocyclic Helix-Threading Peptides for Targeting RNA

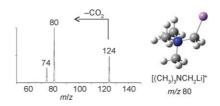
Hanging on by a thread: RNA-binding macrocyclic helix-threading peptides were synthesized by solid-phase ring-closing metathesis. The cyclic peptide shows improved affinity to a target RNA over its linear precursor. This compound also binds a naturally occurring precursor microRNA target and may be valuable for regulating microRNA function.



Nitrogen Ylides

R. A. J. O'Hair,* T. Waters, B. Cao _______ **7048 – 7051**

Sixty Years after Wittig: Gas-Phase Synthesis of Lithium Trimethylammonium Methylide, [(CH₃)₃NCH₂Li]⁺



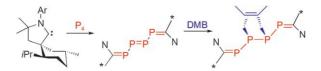
Very Wittig: Collisional activation of the lithiated betaine cation $[(CH_3)_3NCH_2CO_2Li]^+$ (m/z 124) in the gas phase results in decarboxylation to form the lithiated ylide $[(CH_3)_3NCH_2Li]^+$ (m/z 80). Calculations and ion–molecule reactions with water confirm the identity and reactivity of this species.



P₄ Activation

J. D. Masuda, W. W. Schoeller,
B. Donnadieu, G. Bertrand* 7052 – 7055

Carbene Activation of P_4 and Subsequent Derivatization



Broken down and added onto: An enantiomerically pure cyclic (alkyl)- (amino) carbene cleanly activates P_4 , affording highly reactive products that can be further used for the diastereoselective construction of P_4 -containing molecules

that feature phosphorus—carbon bonds (see scheme; DMB = 2,3-dimethylbuta-diene; portions of the products have been omitted, * denotes a stereogenic carbon center).



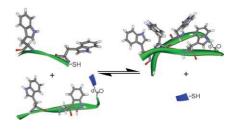
Protein Folding

E. B. Hadley, A. M. Witek, F. Freire, A. J. Peoples,

S. H. Gellman* ______ 7056-7059

Thermodynamic Analysis of β -Sheet Secondary Structure by Backbone Thioester Exchange

No need for references: The conformational stability of β hairpins has been examined by replacing a backbone amide group by a thioester (see picture). The increased flexibility causes a decrease in the β -hairpin stability without changing the structure of the folded conformation and allows the stability of the folded state to be measured under native conditions, without the need for reference compounds for the fully unfolded and folded states.





DMA; R = H: 6 steps, 55% MA and 2'-epi-MA; R = OH: 7 steps, 40%

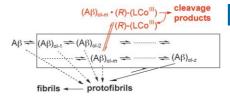
Ironing out plant uptake: The phytosiderophores mugineic acid (MA) and deoxymugineic acid (DMA) were synthesized in a few steps with minimum use of protecting groups and workup/purification procedures (see scheme; Boc: tert-butoxycarbonyl) and their potencies in transporter-mediated iron(III) acquisition were tested. The sufficient supply of these compounds will enable study of the molecular mechanism of iron acquisition and utilization by graminaceous plants.

Iron Acquisition

K. Namba, Y. Murata, M. Horikawa, T. Iwashita, S. Kusumoto* _ 7060 - 7063

A Practical Synthesis of the Phytosiderophore 2'-Deoxymugineic Acid: A Key to the Mechanistic Study of Iron Acquisition by Graminaceous Plants

Clearing the mind: Peptide-cleaving agents for amyloid β -42 (A β_{42}) oligomers (see scheme), the intermediate neurotoxic species in the pathology of Alzheimer's disease, have been obtained from a combinatorial library built using the Co^{III} complex of 1,4,7,10-tetraazacyclododecane as the reaction center. Effective cleavage of the $A\beta_{42}$ oligomers occurs at submicromolar concentrations of the agents.



Peptide Cleavage

J. Suh, * S. H. Yoo, M. G. Kim, K. Jeong, J. Y. Ahn, M.-s. Kim, P. S. Chae, T. Y. Lee, J. Lee, J. Lee, Y. A. Jang, E. H. Ko ___ 7064 - 7067

Cleavage Agents for Soluble Oligomers of Amyloid β Peptides

$$CO_2Et$$
 CO_2Et
 CO_2Et
 CO_2Et
 CO_2Et
 CO_2Et
 CO_2Et
 CO_2Et
 CO_2Et

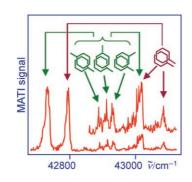
Bicycles built for two: The palladiumcatalyzed intermolecular tandem reaction of propargylic compounds with 2-iodophenols offers an efficient, direct route to spirocyclic compounds with high regioselectivity. The reaction conditions and the scope of the process are examined, and a possible mechanism is proposed.

Tandem Reactions

H.-P. Bi, X.-Y. Liu, F.-R. Gou, L.-N. Guo, X.-H. Duan, X.-Z. Shu, Y.-M. Liang* _ 7068 - 7071

Highly Regioselective Synthesis of Spirocyclic Compounds by a Palladium-Catalyzed Intermolecular Tandem Reaction

It's a gas! Mass-analyzed threshold ionization (MATI) spectroscopy provides high-resolution ionization potentials and low-energy vibrational frequencies of individual conformers of jet-cooled [$(\eta^6$ -PhMe)2Cr]. The signals arising from distinct structural isomers were identified on the basis of DFT calculations and comparison of the [$(\eta^6$ -PhMe)₂Cr] and [$(\eta^6$ -1,3- $Me_2C_6H_4$) (η^6 -PhH)Cr] spectra (see picture).



Ionization Spectroscopy

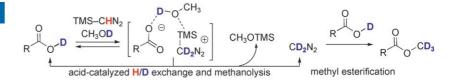
S. Y. Ketkov,* H. L. Selzle, F. G. N. Cloke __ 7072 - 7074

Direct Detection of Individual Bis(arene) Rotational Isomers in the Gas Phase by Mass-Analyzed Threshold Ionization Spectroscopy

Contents

Reaction Mechanisms

Mechanism of Methyl Esterification of Carboxylic Acids by Trimethylsilyldiazomethane



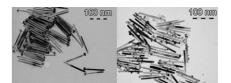
Minimal hazard: A deuterium-labeling study reveals that, contrary to prior assumption, the safe, reliable, and widely adopted method for methyl esterification of carboxylic acids using trimethylsilyldi-

azomethane (TMS-CHN₂) proceeds through the concurrent acid-catalyzed methanolytic liberation of diazomethane (see scheme).

Hybrid Nanorods

Hybrid Co-Au Nanorods: Controlling Au Nucleation and Location

Au Co-ntraire: The growth of gold nanoparticles on magnetic cobalt nanorods could be initiated either selectively on the tips of the nanorods (see picture, left) or nonselectively over the whole nanorod surface (right) by the proper choice of ligand concentration and temperature. Heterogeneous nucleation was selected over galvanic displacement by the choice of the gold(I) precursor.



Copper(III) Intermediates

S. H. Bertz,* S. Cope, D. Dorton, M. Murphy, C. A. Ogle* _____ **7082 – 7085**

Organocuprate Cross-Coupling: The Central Role of the Copper(III) Intermediate and the Importance of the Copper(I) Precursor

Me₂CuLi∙LiX -100 °C Et-I rapid injection

$$\begin{bmatrix} & \text{Me} \\ | \\ \text{Et-Cu-X} \\ | \\ | \\ \text{Me} \end{bmatrix}^- \text{Li}^+$$

X = I, CN, SCN, SPh

X = I, CN, SCN, SPh, Me

Cu^{III} in focus: The key intermediate in copper-mediated cross-coupling reactions has long been believed to be a "copper-(III) intermediate". Investigation of reactions of a variety of methyl Gilman reagents Me₂CuLi-LiX with EtI using rapid-

injection NMR spectroscopy conditions reveals a number of formally Cu^{III} tetracoordinate square-planar intermediates (see scheme) with a surprising range of stabilities.

Natural Product Synthesis

S. Lanners, H. Norouzi-Arasi, X. J. Salom-Roig,

G. Hanquet* ______ 7086-7089

A Convergent Strategy for the Pamamycin Macrodiolides: Total Synthesis of Pamamycin-607, Pamamycin-593, and Pamamycin-621D Precursors

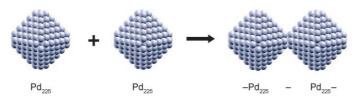
A convergent total synthesis of pamamycin-607 (1), isolated from *Streptomyces alboniger*, was achieved by an *E–Z* isomerization of a tetrahydrofuran alkylidene and a regio- and diastereoselective solvent-dependent *cyclo*-C₆H₁₁BCl/Et₃N-mediated aldol reaction as the key steps. The second key step was extended to other ketones, opening the route to new pamamycin macrodiolides, for example, pamamycin-593 and pamamycin-621D.



Hidden benefits: The enantioselective organocatalytic protonation of silyl enolates has been achieved by using readily available cinchona alkaloid catalysts (1) and a latent source of HF that delivers "at will" the active catalytic hydrogen fluoride salt (1-HF). This approach leads to enantioselective proton transfer with high enantioselectivities of up to 92% under mild, neutral, and metal-free conditions (see scheme, TMS = trimethylsilyl).

Organocatalysis

- T. Poisson, V. Dalla, F. Marsais, G. Dupas, S. Oudeyer, V. Levacher* ___ 7090 - 7093
- Organocatalytic Enantioselective Protonation of Silyl Enolates Mediated by Cinchona Alkaloids and a Latent Source of HF



Model nanowires $(Pd_n)_x$ were constructed from isolated cuboctahedral clusters Pd, (n=38, 79, 140, 225), as depicted for n = 225. Periodic density functional calculations show that the elasticity of the

nanoparticles plays a key role in the selfassembly mechanism. The results are also relevant to sintering in the catalysts by supported metal nanoparticles.

Nanowire Self-Assembly

- F. Viñes, F. Illas,* K. M. Neyman* _ 7094 – 7097
- On the Mechanism of Formation of Metal Nanowires by Self-Assembly

Steric screening: In alkylations of metalated nitriles containing vicinal methyl groups and a trisubstituted C=C bond, the butene moiety screens electrophilic attack from one diastereotopic face as the quaternary stereocenter is installed (see

scheme; LDA = LiNiPr₂). Excellent stereoselectivity is maintained with a wide range of electrophiles to yield acyclic nitriles with contiguous tertiary and quaternary stereocenters.

Asymmetric Induction

F. F. Fleming,* W. Liu, S. Ghosh, O. W. Steward ______ 7098 - 7100

Metalated Nitriles: Internal 1,2-Asymmetric Induction

Better than Cu, Pd, and Fe catalysts: The rhodium-catalyzed reaction of alkynyl oxiranes with arylboronic acids provides synconfigured α -allenols with excellent diastereoselectivity. Precoordination of the

Angew. Chem. Int. Ed. 2007, 46, 6937-6948

oxygen atom of the oxirane ring to rhodium is assumed to contribute to the high stereoselectivity as well as high reactivity.

α-Allenol Synthesis

T. Miura, M. Shimada, S.-Y. Ku, T. Tamai, M. Murakami* _____ 7101 - 7103

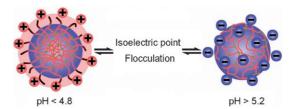
Stereoselective Synthesis of $\alpha ext{-Allenols}$ by Rhodium-Catalyzed Reaction of Alkynyl Oxiranes with Arylboronic Acids

Contents

Stimuli-Responsive Polymers

X. Shen, L. Zhang, X. Jiang,* Y. Hu, J. Guo _______ **7104-7107**

Reversible Surface Switching of Nanogel Triggered by External Stimuli



Inside out and back again: A novel nanogel composed of two biocompatible components, namely chitosan and ethylenediaminetetraacetic acid, is presented and shows novel surface switching of both composition and charge in response to

pH changes in the medium (see picture). The pH-dependent surface switch of this nanogel is fully reversible and the particle integrity is maintained in the entire pH range owing to the gel nature of the system.

Reaction Mechanisms

S. D. Lotesta, S. Kiren, R. R. Sauers, L. I. Williams* _______ 7108 – 7111

Spirodiepoxides: Heterocycle Synthesis and Mechanistic Insight

$$H_3C$$
 H_3C
 H_3C

In concert but out of sync: Reactions of spirodiepoxides (SDEs) with an amide, amidine, and thioamide and the first crystal structure of an SDE are reported (see scheme for reaction with amide; DMDO = 2,2-dimethyldioxirane). Nucleo-

philic SDE opening is rationalized in terms of a reactivity continuum involving the concerted, asynchronous opening of both epoxides, which is facilitated by coordination to the oxygen atom destined to become the hydroxy group.

Multielectron Reduction

H. Tannai, T.-a. Koizumi, T. Wada, K. Tanaka* _______ 7112 - 7115

Electrochemical and Photochemical Behavior of a Ruthenium(II) Complex Bearing Two Redox Sites as a Model for the NAD+/NADH Redox Couple

Four by four: The mononuclear ruthenium(II) complex $[1]^{2+}$ is reversibly converted into the four-electron-reduced form $[1-H_4]^{2+}$ through electrochemical and photochemical redox reactions in aqu-

eous solution. The 2,6-bis (benzo[b]-1,5-naphthyridin-6-yl)-4-tert-butylpyridine ligand acts alteratively as a reservoir/source of four electrons or four protons.

Nickel Cyanide

S. J. Hibble,* A. M. Chippindale,*
A. H. Pohl, A. C. Hannon ____ 7116-7118

Surprises from a Simple Material—The Structure and Properties of Nickel Cyanide

$$\begin{array}{c}
\text{Ni} \stackrel{\text{1.87 A}}{\longrightarrow} C \equiv N \stackrel{\text{2.05 A}}{\longrightarrow} \text{Ni} \\
+ \text{H}_2\text{O} \downarrow \uparrow - \text{H}_2\text{O} \\
\text{Ni} \stackrel{\text{1.86 A}}{\longrightarrow} C \equiv N \stackrel{\text{1.86 A}}{\longrightarrow} \text{Ni}
\end{array}$$

The cyanide switch. The bonding of the cyanide ligand of Ni(CN)₂·nH₂O changes dramatically on dehydration to Ni(CN)₂, equalizing the Ni–C and Ni–N bonds and switching the Ni²⁺ ion bound to nitrogen from high spin to low spin. Total neutron diffraction studies on Ni(CN)₂ provide for the first time accurate structural data on this simple layered metal cyanide. Ni(CN)₂ is a model two-dimensional negative thermal-expansion material.





Smells like roses: The catalytic enantioselective ketonization of two isolated enols was successful and made possible the discussion of the important mechanistic implications of these findings. The indirect enolate protonation occurs via enols and higher-order mixed aggregates (see scheme). The reaction was used to synthesize the rose-smelling fragrance compound (S)- α -damascone.

Enantioselective Protonation



C. Fehr* . 7119 - 7121

Catalytic Enantioselective Tautomerization of Isolated Enols

A question of the ligand: The chemoselectivity of the rhodium-catalyzed addition of AlMe₃ to cyclohex-2-enone is guided by the type of ligand used. Whereas use of an achiral {Rh(cyclooctadiene)} complex leads to a 1,4-addition, use of a {Rh(binap)} species gives highly enantioselective 1,2-additions. This

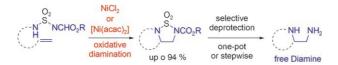


unprecedented reaction can be used for stereoselective 1,2-methylations and arylations of cyclic enones (see scheme).

Asymmetric Catalysis

J. Siewert, R. Sandmann, P. von Zezschwitz* _ 7122 - 7124

Rhodium-Catalyzed Enantioselective 1,2-Addition of Aluminum Organyl Compounds to Cyclic Enones



Nickel can oxidize, too! Nickel(II) salts such as nickel chloride and nickel acetylacetonate catalyze the intramolecular diamination of alkenes with urea and guanidine derivatives as well as sulfamides as nitrogen sources. The latter

represent particularly attractive starting materials, as they allow for a selective and convenient liberation of the diamines from the oxidation products (see scheme).

Oxidation Catalysis with Nickel

K. Muñiz,* J. Streuff, C. H. Hövelmann, A. Núñez ______ 7125 - 7127

Exploring the Nickel-Catalyzed Oxidation of Alkenes: A Diamination by Sulfamide Transfer



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).

The issues for September 2007 appeared online on the following dates Issue 33: August 13. · Issue 34: August 20. · Issue 35: August 28. · Issue 36: September 4.

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Apology

Hydrogen Peroxide Triggered Prochelator Activation, Subsequent Metal Chelation, and Attenuation of the Fenton Reaction

Y. Wei, M. Guo* ______ 4722-4725

Angew. Chem. Int. Ed. 2007, 46

DOI 10.1002/anie.200604859

After consultations with the Editors of Angewandte Chemie the authors would like to apologize that reference [17], which deals with work directly related to this manuscript, is cited in a way which may not indicate the full relevance of this work. To put this citation into the correct context the authors would like to add the sentence "A boronic ester analogue BSIH has just been reported by Franz et al.[17]" This sentence should be placed in the introduction after "(SIH)" on page 4722, 2nd column, paragraph 3, line 4. The authors apologize to the readers, referees, and Editors of Angewandte Chemie, and to the authors of reference [17] for this oversight.

[17] L. K. Charkoudian, D. M. Pham, K. J. Franz, J. Am. Chem. Soc. 2006, 128, 12424.

Corrigendum

Reformatsky Reactions Meet Catalysis and Stereoselectivity

_____ 2568–2571 P. G. Cozzi* __

Angew. Chem. Int. Ed. 2007, 46

DOI 10.1002/anie.200604344

It has been brought to the author's attention that Scheme 6 in their Highlight was incorrectly drawn. The correct Scheme 6 is provided below. The author apologizes for the oversight.

Scheme 6. A Reformatsky reaction performed on a large scale in industry. NMP = N-methyl-2-pyrrolidinone.

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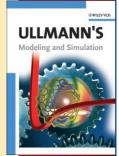
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