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:

A.-M. L. Fuller, D. A. Leigh, P. J. Lusby*
One Template, Multiple Rings: Controlled Iterative Addition of Macrocycles onto a Single Binding Site Rotaxane Thread

*H. Matsuzawa, Y. Miyake, Y. Nishibayashi**
Ruthenium-Catalyzed Enantioselective Propargylation of Aromatic Compounds with Propargylic Alcohols via Allenylidene Intermediates

*C. Fehr**
Catalytic, Enantioselective Tautomerization of Isolated Enols

*J. S. J. McCahill, G. C. Welch, D. W. Stephan**
Reactivity of Frustrated Lewis Pairs: Three Component Reactions of Phosphine, Borane, and Olefins

H. Braunschweig, M. Forster, K. Radacki, F. Seeler, G. R. Whittell*
Stepwise Intermetal Borylene Transfer: Synthesis and Structure of Mono- and Dinuclear CoBorylene Complexes

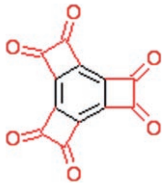
A. Scarso, L. Pellizzaro, O. De Lucchi, A. Linden, F. Fabris**
Gas Hosting in Enantiopure Self-Assembled Oximes

Obituary

Books

Highlights

Benzynes



Some fine arynes: Elimination of triflate followed by [2+2] cycloaddition with ketene silyl acetals facilitates the formation of highly strained benzynes with one or two annulated cyclobutane rings. A prominent example based on this chemistry is the synthesis of the novel oxocarbon $C_{12}O_6$ (see structure).

Essays

Chirality

Chirality, the key concept first proposed by Kelvin, was reintroduced in textbooks in the mid-1960s. Since then, it has been the source of much reflection and inspiration. This Essay traces the nonchemical origins of the concept and its semantic connotations, which not only enrich the language of chemistry but also have ramifications in, for example, philosophy.

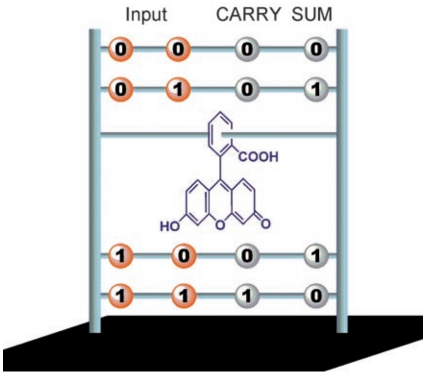
Contents

Minireviews

Molecular Logic Elements

U. Pischel* ______________ **4026 – 4040**

Chemical Approaches to Molecular Logic Elements for Addition and Subtraction



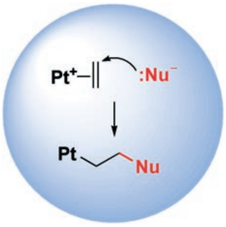
Go figure! Molecules that can add or subtract binary digits are an interesting aspect of the concept of molecular logic. In contrast to silicon-based microprocessors, these molecular devices receive chemical or optical input signals. The picture shows an abacus, one of the oldest devices for calculation, and fluorescein, a universal model of a molecular calculator, interlinked by the truth table of a half adder.

Reviews

Homogeneous Catalysis

A. R. Chianese,* S. J. Lee,
M. R. Gagné ______________ **4042 – 4059**

Electrophilic Activation of Alkenes by Platinum(II): So Much More Than a Slow Version of Palladium(II)



Going platinum: Many metal ions are known for their ability to activate olefins toward nucleophilic attack and platinum(II) complexes are no exception. The wide range of platinum-catalyzed reactions, often complementary to palladium catalysis, includes simple addition to alkenes (hydroamination, hydroarylation, hydroalkylation) and more complex cycloisomerization reactions.

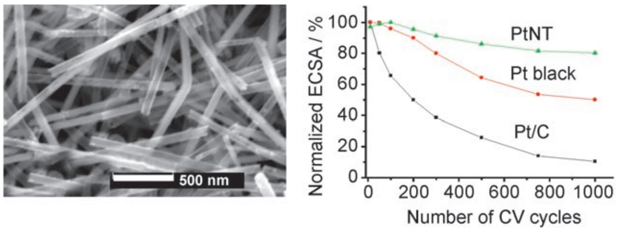
Communications

VIP

Oxygen-Reduction Catalysts

Z. Chen, M. Waje, W. Li,
Y. S. Yan* ______________ **4060 – 4063**

Supportless Pt and PtPd Nanotubes as Electrocatalysts for Oxygen-Reduction Reactions



Staying power: A new class of cathode catalysts based on supportless Pt (see picture, left) and PtPd nanotubes (NTs) is introduced. These materials have remarkable durability (right; CV = cyclic voltammetry, ECSA = electrochemical surface area) and high catalytic activity. They have the potential to circumvent most of the degradation pathways of current Pt/C and Pt-black catalysts.

For the USA and Canada:
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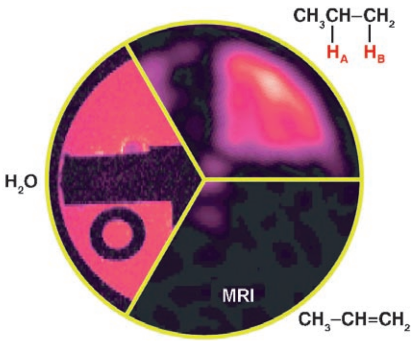
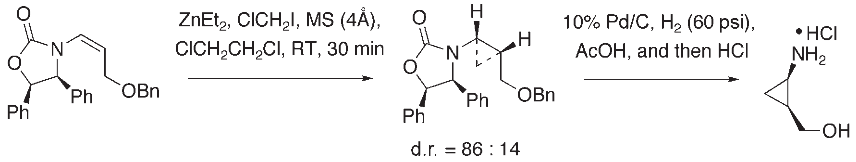


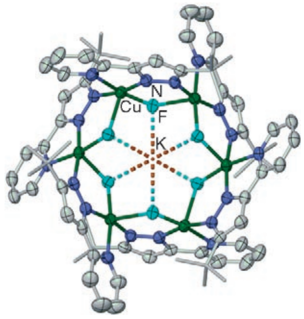
Gas-phase MRI phantom: Magnetic resonance imaging (MRI) in the gas phase was demonstrated using para-hydrogen-induced polarization. H_2 enriched in the para (antiparallel) spin state and propylene gas were flowed over solid-supported Wilkinson's catalyst, and the product, propane gas, was collected in an NMR tube. Enhanced signal intensities were observed in the images of phantoms placed inside the NMR tube (see picture).

Gas-Phase MRI



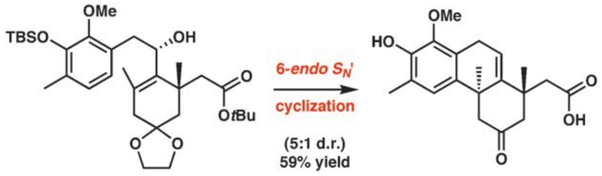
Efficient and practical access to chiral aminocyclopropanes is secured by the title reaction (see example). Both *E* and *Z* enamides undergo the cyclopropanation with high diastereoselectivity (d.r. up to $>95{:}5$). The application of this methodology to the synthesis of biologically significant aminocyclopropanes illustrates the potential of chiral enamides as useful building blocks for stereoselective organic synthesis.

Synthetic Methods



A brimming bowl: The [12]MC-6 fluoro metallacrown (MC) shown in the picture is crystallized both as a metal-free wheel and in complex with Na^+ or K^+ ions. The magnetic and structural properties are only slightly altered upon metal complexation. Opposite faces of the molecule form bowl-shaped cavities, in which H_2O or CH_2Cl_2 molecules are hydrogen-bonded to the F acceptors.

Fluoro Metallacrown Compounds



A smokin' hot cyclization! When the racemic cyclization precursor is heated in neat trifluoroacetic acid, an unusual Friedel–Crafts-type cyclization forms the carbocyclic core of the marine alkaloid zoanthenol containing two all-carbon-substituted quaternary centers. Catalytic asymmetric alkylation allows entry into an enantioselective route.

Natural Products Synthesis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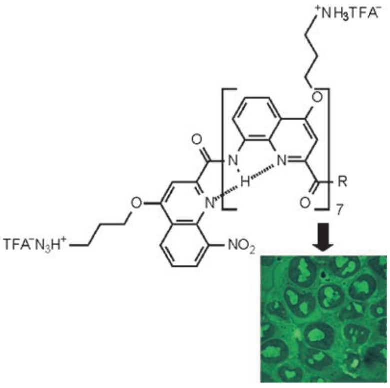
Abiotic but bioactive: Folding aromatic amide oligomers possessing helical structures very different from those of α-peptides, β-peptides, or peptoids nevertheless show comparable abilities to penetrate into cells, as well as low toxicity and complete resistance to protease degradation. TFA^- = trifluoroacetate.

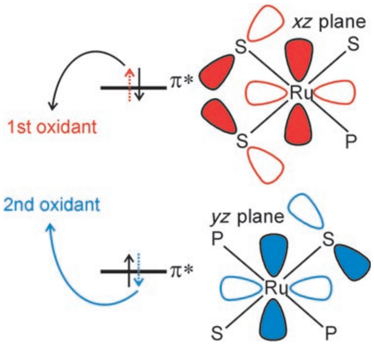


Peptidomimetics

E. R. Gillies, F. Deiss, C. Staedel,
J.-M. Schmitter, I. Huc* ____ 4081 – 4084

Development and Biological Assessment of Fully Water-Soluble Helical Aromatic Amide Foldamers

All alone: The ground state of the oxidized, reactive intermediate $[Ru(dppbt)_3]^+$ (dppbt = 2-diphenylphosphinothiaphenolate) is calculated to be a singlet diradical. The unpaired electrons in the π* orbitals are delocalized over the metal atom and the ligand sulfur atoms. The relative orientation of the half-occupied orbitals inhibits disulfide formation and favors addition of unsaturated hydrocarbons across adjacent sulfur atoms.

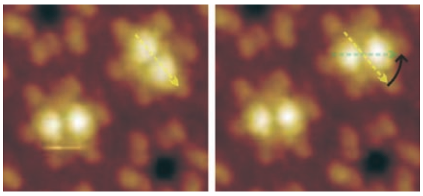


Electronic-Structure Calculations

C. A. Grapperhaus,* P. M. Kozlowski,*
D. Kumar, H. N. Frye, K. B. Venna,
S. Poturovic ____ 4085 – 4088

Singlet Diradical Character of an Oxidized Ruthenium Trithiolate: Electronic Structure and Reactivity

Spinning tops: A supramolecular rotary device, reminiscent of a mechanical rotary switch, was engineered by a bottom-up approach. Self-assembly of a functionalized porphyrin molecule leads to the formation of a porous network that features chiral cavities. These serve as hosts for molecular guests, which can be induced to rotate either thermally or by using the scanning tunneling microscopy tip (see images).

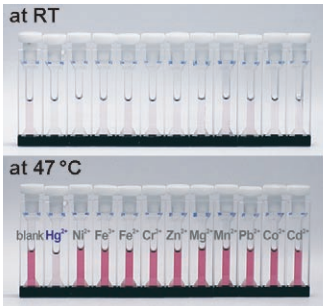


Molecular Devices

N. Wintjes, D. Bonifazi, F. Cheng,
A. Kiebele, M. Stöhr, T. Jung,*
H. Spillmann,*
F. Diederich* ____ 4089 – 4092

A Supramolecular Multiposition Rotary Device

Color is everything: Hg^{2+} in aqueous media is detected by the formation of thymidine–Hg^{2+}–thymidine coordination complexes, which raises the melting temperature of the DNA-hybridized gold nanoparticle probes and thus the temperature at which the probes disperse and effect a purple-to-red color change. The method has very high sensitivity and selectivity, and it provides a simple and fast colorimetric readout (see picture).



Sensors

J.-S. Lee, M. S. Han,
C. A. Mirkin* ____ 4093 – 4096

Colorimetric Detection of Mercuric Ion (Hg^{2+}) in Aqueous Media using DNA-Functionalized Gold Nanoparticles

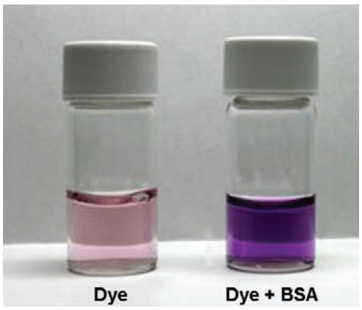
Contents

Protein Detection

Y. Suzuki, K. Yokoyama* ____ **4097 – 4099**

A Protein-Responsive Chromophore Based on Squaraine and Its Application to Visual Protein Detection on a Gel for SDS-PAGE

Dying to know: A visual protein indicator based on squaraine is responsible for a profound color change upon binding to protein in solution, from light pink for the dye alone to deep purple for the dye·BSA complex (see picture; BSA: bovine serum albumin). The detection limit for BSA is 2 μg mL^{-1}, which is about five times higher than that with Coomassie Brilliant Blue as the dye.

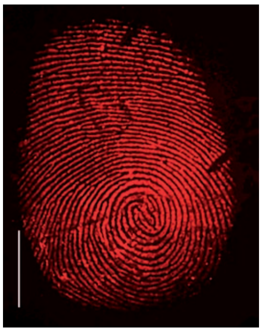


Fingerprinting

R. Leggett, E. E. Lee-Smith, S. M. Jickells, D. A. Russell* ____ **4100 – 4103**

"Intelligent" Fingerprinting: Simultaneous Identification of Drug Metabolites and Individuals by Using Antibody-Functionalized Nanoparticles

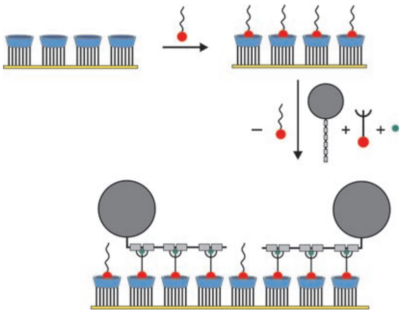
Thumbs up: A method of fingerprinting that enables both identification of an individual and simultaneous determination of the chemical makeup of the sweat deposited in the fingerprint has been determined. Potential applications of this methodology are enormous as the functionalization of nanoparticles with other antibodies enables the specific detection of numerous antigens within a fingerprint.



Host–Guest Systems

M. J. W. Ludden, A. Mulder, R. Tampé,* D. N. Reinhoudt, J. Huskens* ____ **4104 – 4107**

Molecular Printboards as a General Platform for Protein Immobilization: A Supramolecular Solution to Nonspecific Adsorption

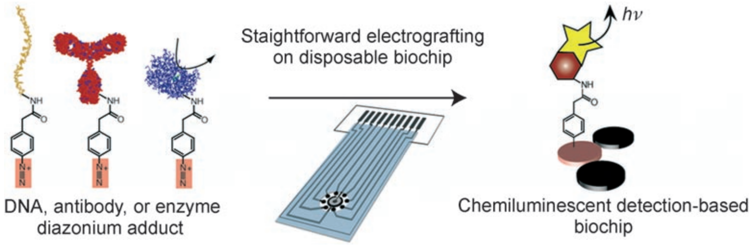


Be specific: A supramolecular adsorbate consisting of an adamantyl group (red) and an oligo(ethylene glycol) chain has been designed to prevent nonspecific protein adsorption at cyclodextrin molecular printboards. The adamantyl group allows specific and reversible interactions. Specific immobilization of proteins (gray) is possible through multivalent orthogonal linkers by effective replacement of the monovalent adsorbate (Ni^{2+} ions (green) may be needed; see picture).

Biochips

B. P. Corgier, A. Laurent, P. Perriat, L. J. Blum, C. A. Marquette* **4108 – 4110**

A Versatile Method for Direct and Covalent Immobilization of DNA and Proteins on Biochips

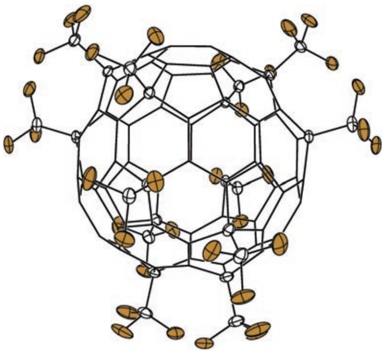


Stuck on sensing: A method is presented for the immobilization of aryl diazonium modified biomolecules by direct electrografting onto the surface of a conducting material to create effective on-chip sensing layers (see picture). Proof of concept is given for both proteins (antibodies, enzymes) and DNA.

Elusive Fullerenes

N. B. Shustova, B. S. Newell, S. M. Miller, O. P. Anderson, R. D. Bolskar, K. Seppelt, A. A. Popov, O. V. Boltalina,* S. H. Strauss* ——— **4111 – 4114**

Discovering and Verifying Elusive Fullerene Cage Isomers: Structures of C_2-p^{11}-(C_{74}-D_{3h})(CF_3)$_{12}$ and C_2-p^{11}-(C_{78}-D_{3h}(5))(CF_3)$_{12}$



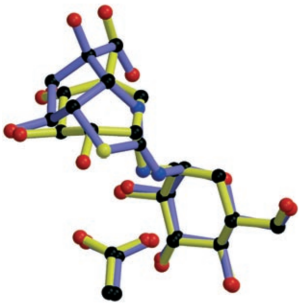
Two in a million: The solid-state structures of C_2-symmetric isomers of $C_{74}(CF_3)_{12}$ (see picture) and $C_{78}(CF_3)_{12}$ have been solved by X-ray crystallography. They verify the structures of the hollow C_{74}-D_{3h} and C_{78}-D_{3h}(5) cages, and exhibit a (*para*)^{11} ribbon of edge-sharing *p*-$C_6(CF_3)_2$ hexagons on the surface of the fullerenes.

Enzyme Structures

R. P. Gibson, T. M. Gloster, S. Roberts, R. A. J. Warren, I. Storch de Gracia, Á. García, J. L. Chiara, G. J. Davies* ——— **4115 – 4119**

Molecular Basis for Trehalase Inhibition Revealed by the Structure of Trehalase in Complex with Potent Inhibitors

Strong inhibitions: The inhibition of trehalases, enzymes which hydrolyze the disaccharide trehalose, is a target for novel antibiotic insecticides. The structures (see picture; C black, N blue, O red, S yellow) of a trehalase in complex with validoxylamine A (yellow) and 1-thiatetrazolin (blue) reveal that the inhibitors tightly bind to the enzyme through hydrogen bonds.

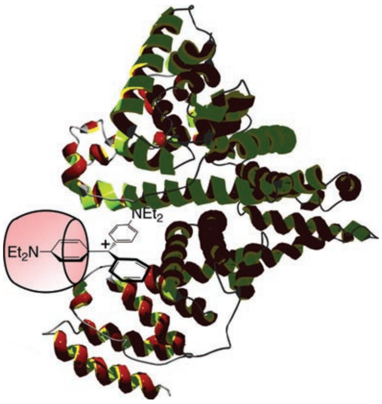


Supramolecular Chemistry

A. C. Bhasikuttan,* J. Mohanty, W. M. Nau,* H. Pal ——— **4120 – 4122**

Efficient Fluorescence Enhancement and Cooperative Binding of an Organic Dye in a Supra-biomolecular Host–Protein Assembly

A factor of 300 enhancement in fluorescence and increased binding is observed when the triphenylmethane dye Brilliant Green binds to bovine serum albumin (BSA) in the presence of the macrocyclic host cucurbit[7]uril (CB7) as a supramolecular "enhancer" (see picture). Thus, a cumulative (multiplicative) fluorescence enhancement occurs compared to the effects observed in the presence of CB7 alone (factor of 6) or BSA alone (factor of 45).

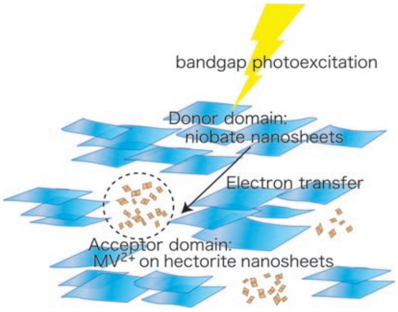


Charge Separation

N. Miyamoto, Y. Yamada, S. Koizumi, T. Nakato* ——— **4123 – 4127**

Extremely Stable Photoinduced Charge Separation in a Colloidal System Composed of Semiconducting Niobate and Clay Nanosheets

The further, the better! Photoinduced charge separation between a semiconducting nanosheet donor and the acceptor methylviologen (MV^{2+}) is greatly stabilized in the presence of hectorite clay nanosheets. The distance between the donor and acceptor, which results from the formation of hectorite microdomains that selectively adsorb MV^{2+} ions, is key for this stabilization (see picture).

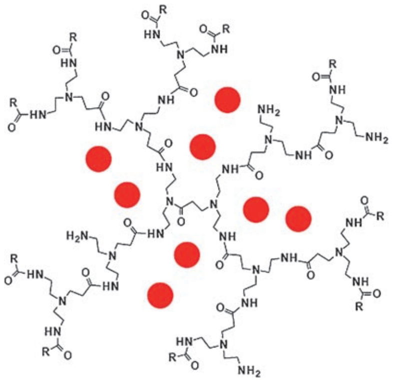


Self-Assembly

C. Liu, C. Gao,* D. Yan* ___ **4128 – 4131**

Honeycomb-Patterned Photoluminescent Films Fabricated by Self-Assembly of Hyperbranched Polymers

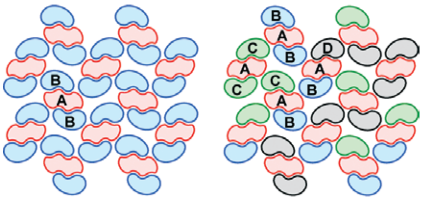
A film to dye for: Honeycomb-patterned films have been fabricated by the self-assembly of amphiphilic hyperbranched poly(amidoamine) on solid substrates. The film thickness can be varied from the nanometer to micrometer scale simply by changing the concentration of the polymer solution. Luminescent films of different colors can be prepared by encapsulating various dyes into the polymer (see picture, R = $(CH_2)_{14}CH_3$, red sphere = dye molecule).



Organic Alloys

M. Dabros, P. R. Emery,
V. R. Thalladi* ___ **4132 – 4135**

A Supramolecular Approach to Organic Alloys: Cocrystals and Three- and Four-Component Solid Solutions of 1,4-Diazabicyclo[2.2.2]octane and 4-X-Phenols (X = Cl, CH_3, Br)

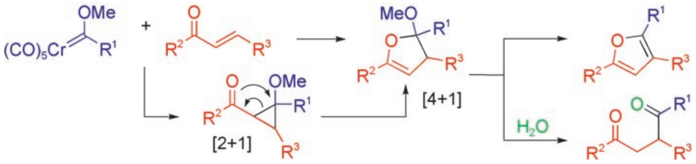


Triple play: The crystallization of 1,4-diazabicyclo[2.2.2]octane (A) with one, two, or three different 4-substituted phenols (B, C, D) leads to cocrystals (for example, AB_2, left) or solid solutions (for example, $A(B,C,D)_2$, right). The repeat units of these multicomponent organic solids are supramolecular assemblies of three molecules.

Synthetic Methods

J. Barluenga,* H. Fanlo, S. López,
J. Flórez ___ **4136 – 4140**

[4+1]/[2+1] Cycloaddition Reactions of Fischer Carbene Complexes with α,β-Unsaturated Ketones and Aldehydes

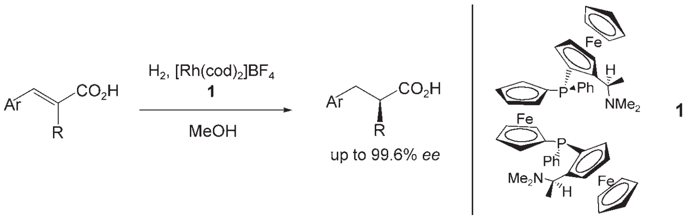


Put two and two together: Fischer carbene complexes and α,β-unsaturated carbonyl compounds smoothly react under thermal conditions to give 2,3-dihydrofurans, and from them furans or 1,4-dicarbonyl compounds were easily accessible (see scheme). This cycloaddition process involves a cyclopropanation reaction followed by rearrangement from the acylcyclopropane to a dihydrofuran.

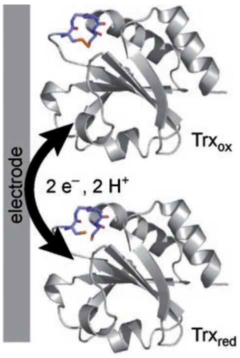
Asymmetric Catalysis

W. Chen,* P. J. McCormack,*
K. Mohammed, W. Mbafor, S. M. Roberts,
J. Whittall ___ **4141 – 4144**

Stereoselective Synthesis of Ferrocene-Based C_2-Symmetric Diphosphine Ligands: Application to the Highly Enantioselective Hydrogenation of α-Substituted Cinnamic Acids



Chirality^3: A new ferrocene-based diphosphine ligand is applied to the asymmetric hydrogenation of α-substituted cinnamic acids. The P-centered-, C-centered-, and planar-chiral ligand $(R_C,R_C,S_{Fc},S_{Fc},S_P,S_P)$-**1** displays unprecedented enantioselectivity in this Rh-catalyzed reaction (see scheme; cod = cycloocta-1,5-diene).



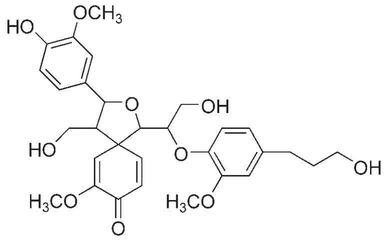
Send and deliver: The thioredoxin (Trx) superfamily of proteins contains small soluble proteins that function as 2 e$^-$/2 H$^+$ electron-transfer agents by virtue of a redox-active disulfide bond. A fully reversible 2 e$^-$ disulfide-bond redox couple can be observed for four different Trx proteins.

Protein Electrochemistry

S. E. Chobot, H. H. Hernandez, C. L. Drennan, S. J. Elliott* **4145 – 4147**

Direct Electrochemical Characterization of Archaeal Thioredoxins

Barking up the right tree: The spirodienone sesquineolignan pinobatol (**1**), a long-time speculated monomeric unit of lignin, was isolated from the 70% aqueous acetone extract of pine (*Pinus sylvestris* L.) bark. Its structure was determined by high-resolution electron ionization mass spectrometry and a variety of NMR spectroscopic techniques.

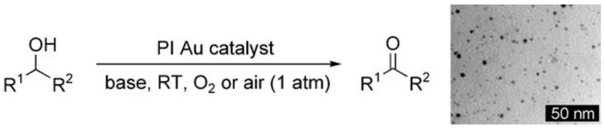


1

Structure Elucidation

J. Sinkkonen,* J. Liimatainen, M. Karonen, K. Wiinamäki, P. Eklund, R. Sjöholm, K. Pihlaja **4148 – 4150**

A Sesquineolignan with a Spirodienone Structure from *Pinus sylvestris* L.



Lock up your gold: Polymer-incarcerated gold nanoclusters (PI Au) were synthesized by microencapsulation of gold nanoclusters and cross-linking using a copolymer based on polystyrene (see TEM image). The nanoclusters could be used to catalyze the aerobic oxidation of alcohols to aldehydes and ketones under atmospheric conditions at room temperature, and additionally could be reused with little loss of activity.

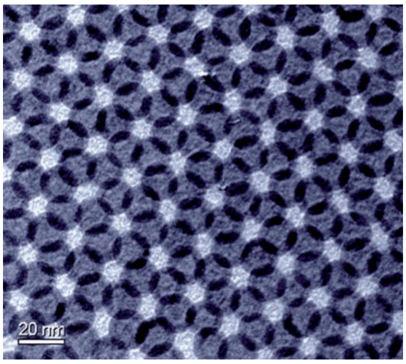
Heterogeneous Catalysis

VIP

H. Miyamura, R. Matsubara, Y. Miyazaki, S. Kobayashi* **4151 – 4154**

Aerobic Oxidation of Alcohols at Room Temperature and Atmospheric Conditions Catalyzed by Reusable Gold Nanoclusters Stabilized by the Benzene Rings of Polystyrene Derivatives

Controlled oxidation of amorphous core–shell Fe–Fe$_3$O$_4$ nanoparticles in a simple solution-phase process affords monodisperse hollow Fe$_3$O$_4$ nanoparticles. Self-assembly of the monodisperse hollow Fe$_3$O$_4$ nanoparticles leads to superlattice arrays (see TEM image). The synthesis offers a general approach to hollow iron oxide and core–shell–void Fe–Fe$_3$O$_4$ nanoparticles that may have potential applications in catalysis and high-frequency electromagnetic devices.

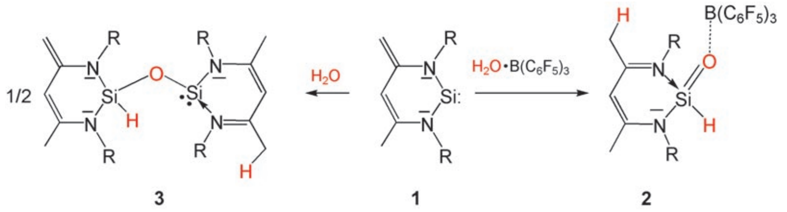


Hollow Nanoparticles

S. Peng, S. Sun* **4155 – 4158**

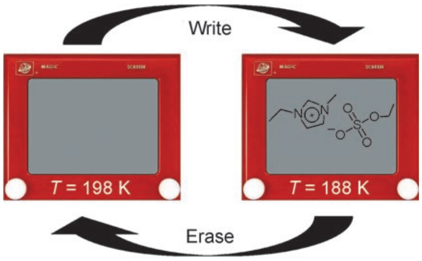
Synthesis and Characterization of Monodisperse Hollow Fe$_3$O$_4$ Nanoparticles

Silicon Chemistry



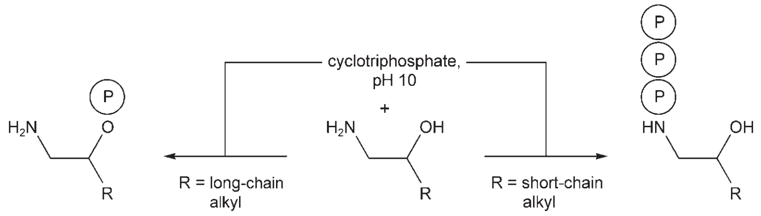
Kipping's dream has (almost) become reality with the first isolable silanone-like complex **2**, prepared by borane-assisted addition of water to the stable silylene **1**. The short Si–O bond in **2** points to considerable Si=O character. In contrast, treatment of **1** with water in the absence of a borane leads to the crystalline siloxy silylene **3**, an unprecedented mixed-valent disiloxane with di- and tetravalent silicon atoms ($R = 2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$).

Ionic Liquids



The write way: A technique for high-resolution rewritable image formation has been derived by using frozen ionic liquids as a temperature-controllable canvas that allows the simple erasure of data. This technique is very flexible as the physicochemical properties of ionic liquids can be fine-tuned through manipulation of the chemical/structural composition of the individual ions.

Amino Alcohol Phosphorylation

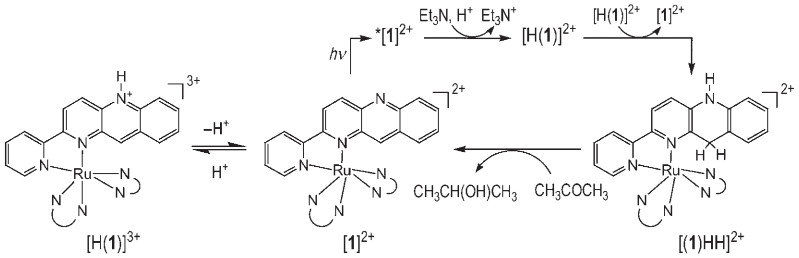


The long and the short of it: In water, long-chain β-hydroxy-*n*-alkylamines are converted to their *O*-monophosphates by reaction with cyclotriphosphate. With short-chain β-hydroxy-*n*-alkylamines, *N*-triphosphates are formed instead. The difference results from the formation of surfactant assemblies from the long-chain compounds. This surfactant control of reactivity may be of relevance to the prebiotic formation of amphiphiles. Ⓟ: phosphate unit.

Hydride Generation

D. Polyansky, D. Cabelli, J. T. Muckerman,
E. Fujita,* T. Koizumi, T. Fukushima,
T. Wada, K. Tanaka* ______ **4169 – 4172**

Photochemical and Radiolytic Production of an Organic Hydride Donor with a Ru^{II} Complex Containing an NAD$^+$ Model Ligand



Role model: The photochemical and electrochemical properties of a polypyridylruthenium complex with an NAD$^+$/NADH (NAD$^+$ = nicotinamide adenine dinucleotide) model ligand, [Ru(bpy)$_2$(pbn)]$^{2+}$ ([**1**]$^{2+}$; bpy = 2,2′-bipyridine, pbn = 2-(2-pyridyl)benzo[*b*]-1,5-naphthyridine), were investigated. When solutions containing [**1**]$^{2+}$ and triethylamine are irradiated with visible light, [(**1**)HH]$^{2+}$ is produced cleanly (see scheme).

Carbohydrates

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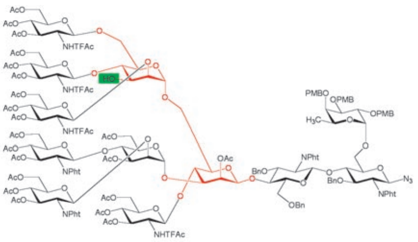
C. Unverzagt* ______ **4173 – 4175**

Synthesis of Pentaantennary N-Glycans with Bisecting GlcNAc and Core Fucose



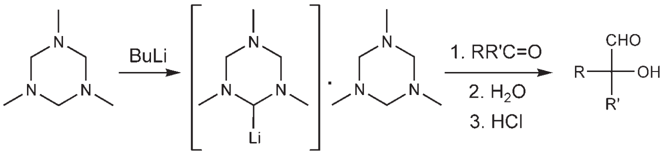
Bn=benzyl, Pht=phthalimido, PMB=*p*-methoxybenzyl
TFAc=trifluoroacetyl

Always use protection? The omission of a single protecting group led to the convergent synthesis of the highly branched dodecasaccharide N-glycan that contains two neighboring tetrasubstituted mannoside groups. A serendipitous finding led to the identification of the key protecting group in oligosaccharide building blocks for the optimized synthesis of N-glycans.

Alkyl Lithium Compounds

D. Bojer, I. Kamps, X. Tian, A. Hepp,
T. Pape, R. Fröhlich,
N. W. Mitzel* ______ **4176 – 4179**

Carbanions with Two N Substituents: Nucleophilic Acyl-Group-Transfer Reagents



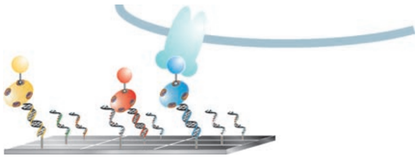
Without mercury or thallium: A new umpoled nucleophilic acylation reagent is formed in the direct deprotonation of 1,3,5-trimethyl-1,3,5-triazacyclohexane with butyllithium. The carbanionic center is flanked by two amino groups, even though lithiation at this position is expected to be disfavored (see scheme).

Microarrays

H. Schroeder, B. Ellinger, C. F. W. Becker,
H. Waldmann,
C. M. Niemeyer* ______ **4180 – 4183**

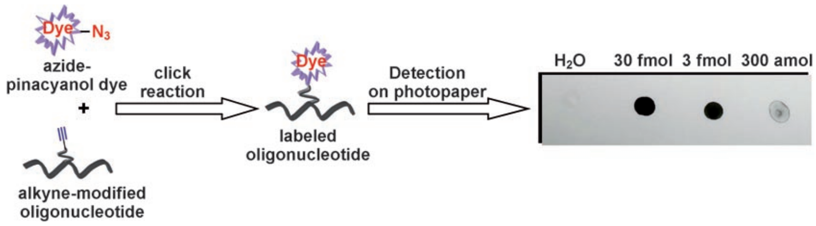
Generation of Live-Cell Microarrays by Means of DNA-Directed Immobilization of Specific Cell-Surface Ligands

Everything in its place: The DNA-directed immobilization of specific cell-surface ligands on a DNA microarray enables the generation of positionally encoded arrays of live cells. Such arrays can be used for fundamental research in molecular cell biology or as a screening platform in the area of drug development



Contents

DNA Detection



All there in black and white: DNA labeled with spectral sensitizers applied to commercially available photopaper allows the detection of oligonucleotides with extreme sensitivity. The detection of the DNA with the help of black and white photography is shown in the picture (ODN = oligodeoxyribonucleotide).

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

Corrigendum

High Turnover Numbers for the Catalytic Selective Epoxidation of Alkenes with 1 atm of Molecular Oxygen

Y. Nishiyama, Y. Nakagawa
N. Mizuno* ________ **3639–3641**

Angew. Chem. Int. Ed. **2001**, *40*

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On the basis of several repeat experiments following publication of their original report, the authors would like to correct their statement on page 3639 (paragraph 3, lines 3–4) of their Communication from “The average carbon balance for six runs was 100 ± 8 %” to “The average carbon balance was 85 ± 15 %”. The authors suggest that the average carbon balance is lower than that stated originally as a result of some contribution of autoxidation.