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

*D. Kim, E. Kim, J. Kim, K. M. Park, K. Baek, M. Jung, Y. H. Ko, W. Sung, H. S. Kim, J. H. Suh, C. G. Park, O. S. Na, D.-k. Lee, K. E. Lee, S. S. Han, K. Kim**
Direct Synthesis of Polymer Nanocapsules with a Noncovalently Tailorable Surface

*T. Tsukahara, A. Hibara, Y. Ikeda, T. Kitamori**
NMR Study on Water Confined in Extended Nanospaces

*C. Filser, D. Kowalczyk, C. Jones, M. Wild, U. Ipe, D. Vestweber, H. Kunz**
Synthetic Glycopeptides with Varied Sialyl Lewis^x Structures as Cell-Adhesion Ligands for E-Selectin

*J. Glöckler, S. Klützke, W. Meyer-Zaika, A. Reller, F. J. García-García, H.-H. Strehblow, P. Keller, E. Rentschler, W. Kläui**
Towards Nanostructured Water-Soluble and Catalytically Active Rhodium Clusters

R. Fischer, M. Gärtner, H. Görls, L. Yu, M. Reiher, M. Westerhausen**
Synthesis and Properties of the THF Solvates of Extremely Soluble Bis(2,4,6-trimethylphenyl)calcium and Tris(2,6-dimethoxyphenyl)dicalcium Iodide

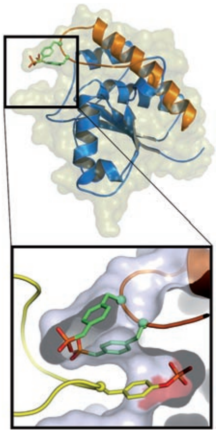
News

Books

Highlights

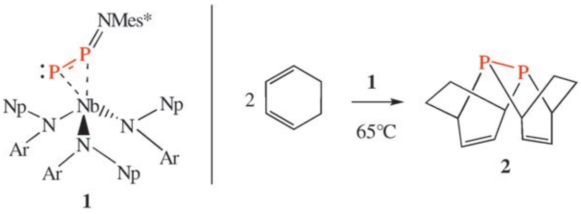
Protein Modification

Chop and change: Techniques that combine chemistry and biology for the modification of proteins have proved themselves to be a good means to study protein function. Expressed protein ligation (EPL), with the help of preparative amounts of phospholated tyrosinephosphatases, prenylated variants of Rab-GTPase Ypt1, biochemically characterized the influence of phosphorylation on the function of phosphatases (see picture; blue: phosphatase; orange: synthetic peptide).



Contents

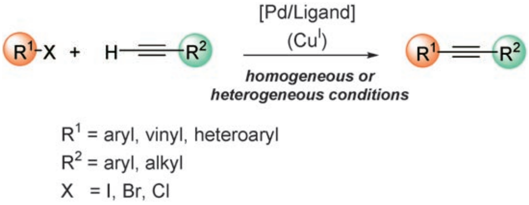
Diphosphorus



A P_2-transfer agent: The niobium complex **1** contains the ligand η^2-P=P=N-Mes*, which can be considered as a diphosphorus-substituted organic azide (Mes* = 2,4,6-tBu$_3C_6H_2$, Np = $CH_2C(CH_3)_3$, Ar = 3,5-$Me_2C_6H_3$). The P_2 unit released upon thermolysis of **1** is cleanly transferred to 1,3-cyclohexadiene, giving the tetracycle **2**.

Reviews

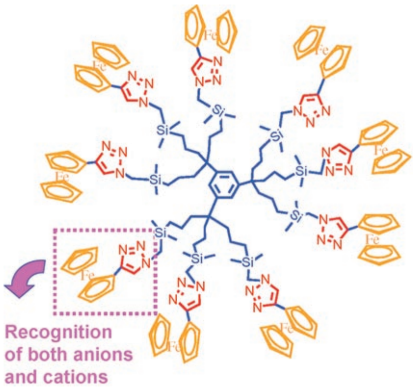
C–C Coupling



Direct alkynylation of C(sp^2) halides or corresponding substrates with terminal alkynes, both in homogeneous and heterogeneous phases, can be achieved by the highly efficient palladium catalyst systems described in this Review. Recycling methods, ligand-free systems, innovative coupling partners, and new activation processes are also discussed.

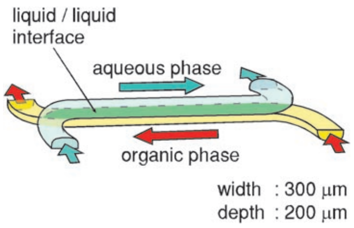
Communications

Dendrimer Sensors

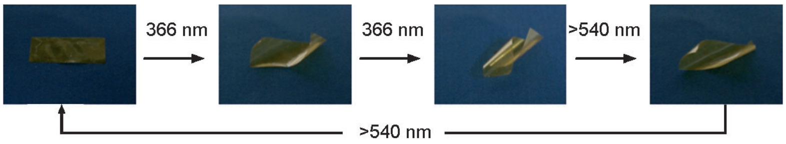


Clickety click: Click dendrimers, including the first click metallodendrimers, are synthesized in the presence of a stoichiometric amount of copper(I). The 1,2,3-triazolylferrocenyl dendrimers (see picture) are selective electrochemical sensors for both transition-metal cations and oxo anions.

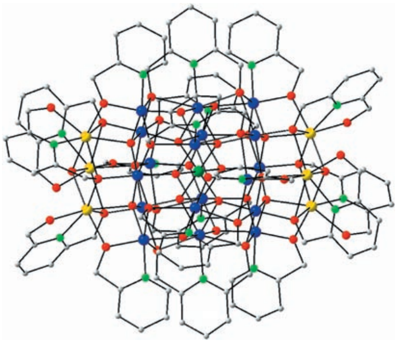
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH PO Box 191161, D 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc. 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 5685/5168 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



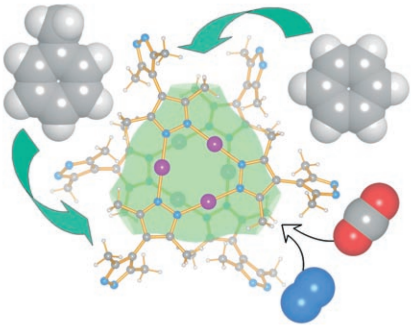
By modifying the walls of a glass microchannel so that one side is hydrophilic and the other hydrophobic, countercurrent laminar flow of an organic phase relative to an aqueous phase is effected (see picture). This system is applied to the efficient extraction of a cobalt complex from toluene into water.



Bending over backwards: Ferroelectric liquid-crystalline (LC) elastomer films with a high LC order and low glass transition temperature bend when irradiated with light (see picture). At 366 nm the films bend toward the actinic light source along the alignment direction of the mesogens, and they recover their initial flat state after exposure to visible light. The mechanical force generated by photoirradiation reaches about 220 kPa.



Spin doctoring: The already high spin of $S=51/2$ of a Mn_{25} complex has been pushed even higher, by approximately 20%, to $S=61/2$ by targeted substitution of the azide ligands with an N,O-chelating group. This significant adjustment, or tweaking, of the spin suggests the general possibility that a given type of complicated, high-nuclearity, high-spin molecule can exhibit differing ground states by appropriate modification of the peripheral ligation.

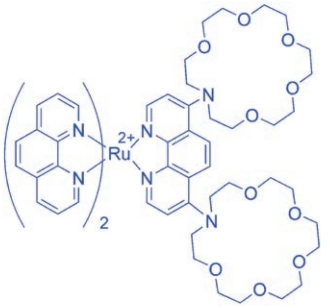


Smart pores: A 3D coordination polymer $[Ag_2(Me_4bpz)]$ ($H_2Me_4bpz=3,3',5,5'$-tetramethyl-4,4'-bipyrazole) can not only reversibly adsorb and desorb CO_2 and N_2 (see picture: Ag pink, C gray, O red N blue) but also benzene and toluene despite its aperture being too small for these molecules. The host framework simultaneously expands some cavities and shrinks others to accommodate different aggregates of the arene molecules.

Multi-Ion Analysis

M. Schmittel,* H.-W. Lin ______ **893 – 896**

Quadruple-Channel Sensing: A Molecular Sensor with a Single Type of Receptor Site for Selective and Quantitative Multi-Ion Analysis



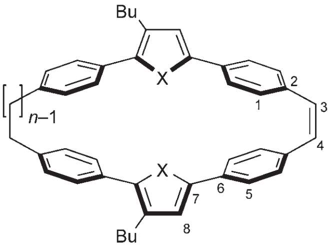
All together now: A "lab on a molecule" for selective and quantitative multi-ion analysis was established. The ruthenium complex, which contains only a single type of recognition site, is a chemosensor for Pb^{2+}, Hg^{2+}, and Cu^{2+} ions by using quadruple-channel detection (UV/Vis, luminescence, electrogenerated chemiluminescence, and cyclic voltammetry).

Nonlinear Optics

H.-C. Lin, W.-Y. Lin, H.-T. Bai, J.-H. Chen, B.-Y. Jin, T.-Y. Luh* ______ **897 – 900**

A Bridging Double Bond as an Electron Acceptor for Optical Nonlinearity of Furan-Containing [*n*.2]Cyclophenes

All in the twist: Unusually large Stokes shifts and nonlinear optical properties are exhibited by furan-containing teraryl cyclophene derivatives (see picture). These cyclophenes have neither particularly strong electron-donating nor electron-withdrawing groups and have low polarity. DFT calculations have shown that the unusual photophysical properties are dictated by twisted π systems in the teraryl systems and the bridging double bond.

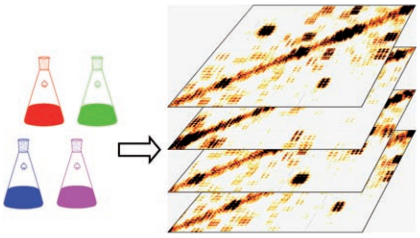


NMR Spectroscopy

F. C. Schroeder,* D. M. Gibson, A. C. L. Churchill, P. Sojikul, E. J. Wursthorn, S. B. Krasnoff, J. Clardy ______ **901 – 904**

Differential Analysis of 2D NMR Spectra: New Natural Products from a Pilot-Scale Fungal Extract Library

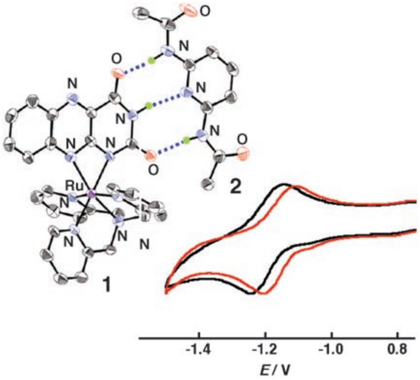
A 3D look at 2D spectra: Two previously unreported indole alkaloids could be rapidly identified from a library of unfractionated fungal extracts by using a newly developed protocol for the differential analysis of arrays of 2D NMR spectra (see picture). The technique thus represents an effective tool for the non-discriminatory characterization of secondary-metabolite mixtures.



Coordination Modes

S. Miyazaki, K. Ohkubo, T. Kojima,* S. Fukuzumi* ______ **905 – 908**

Modulation of Characteristics of a Ruthenium-Coordinated Flavin Analogue That Shows an Unusual Coordination Mode

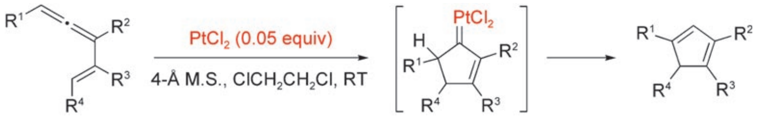


Hallo⁻ hallo⁻! A ruthenium(II) complex (**1**) with the flavin analogue alloxazine (H_2allo) has revealed that the ligand anion (Hallo⁻) forms a four-membered chelate ring. This unprecedented coordination mode of Hallo allows it to form hydrogen bonds with a complementary receptor (e.g. **2**), allowing the effects of hydrogen bonding on the redox behavior and electronic structure of a ruthenium-bound Hallo radical to be studied.

Cyclopentadiene Synthesis (1)

H. Funami, H. Kusama,
N. Iwasawa* ______ **909 – 911**

Preparation of Substituted Cyclopentadienes through Platinum(II)-Catalyzed Cyclization of 1,2,4-Trienes

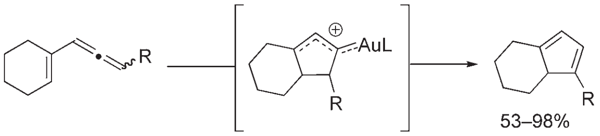


A pinch of platinum... Platinum(II)-catalyzed cyclization of 1,2,4-trienes proceeds under mild conditions to give well-defined, highly substituted cyclopentadienes in good yield. The reaction was confirmed to proceed through α,β-unsaturated platinum–carbene complex intermediates (see scheme).

Cyclopentadiene Synthesis (2)

J. H. Lee, F. D. Toste* ______ **912 – 914**

Gold(I)-Catalyzed Synthesis of Functionalized Cyclopentadienes



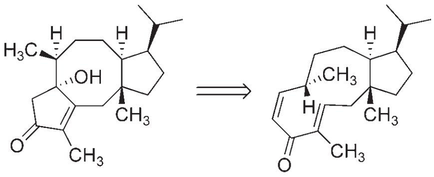
... or a touch of gold: Electrocyclization of the pentadienyl cation produced on coordination of cationic phosphinegold(I) to vinyl allenes results in the regioselective formation of highly functionalized cyclopentadienes. The regioselectivity of the reaction is consistent with an intramolecular 1,2-hydrogen shift of a gold(I)–carbenoid intermediate (see scheme).

Diterpene Total Synthesis

D. R. Williams,* L. A. Robinson,
C. R. Nevill, J. P. Reddy ______ **915 – 918**

Strategies for the Synthesis of Fusicoccanes by Nazarov Reactions of Dolabelladienones: Total Synthesis of (+)-Fusicoauritone

Attaining closure: A synthetic pathway leading to (+)-fusicoauritone (**1**) is highlighted by the use of a Julia condensation for preparation of an eleven-membered-dolabelladienone precursor for subsequent Nazarov cyclization to yield the 5-8-5 tricyclic diterpene skeleton.



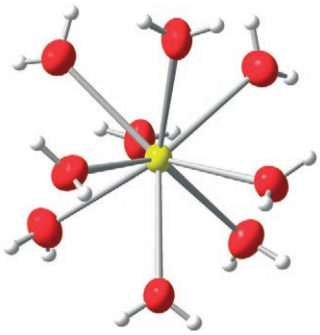
fusicoauritone (**1**)

Transplutonium Chemistry

P. Lindqvist-Reis,* C. Apostolidis,
J. Rebizant, A. Morgenstern, R. Klenze,
O. Walter, T. Fanghänel,
R. G. Haire ______ **919 – 922**

The Structures and Optical Spectra of Hydrated Transplutonium Ions in the Solid State and in Solution

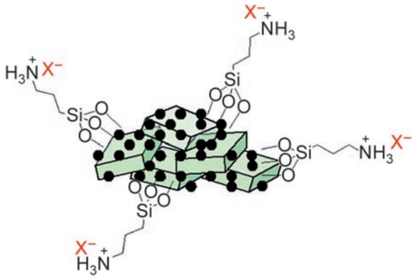
Stable nine-coordination: X-ray diffraction reveals highly symmetrical $[M(H_2O)_9]^{3+}$ entities for the actinides americium and curium in single crystals of their triflate salts (see picture, yellow M, red O). Comparison of absorption spectra in solution confirm that these transplutonium ions are large enough to remain ninefold coordinated also in aqueous solution.



Sensors

A. Gómez-Avilés, M. Darder, P. Aranda,
E. Ruiz-Hitzky* ______ **923 – 925**

Functionalized Carbon–Silicates from Caramel–Sepiolite Nanocomposites

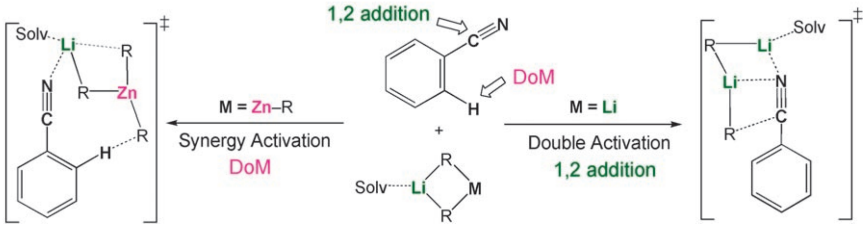


Hybrid compounds that are electrical conductors and can recognize ions are prepared from a carbohydrate (sucrose) and a fibrous magnesium silicate (sepiolite). Microwave and conventional heating convert these starting materials into carbonaceous nanocomposites, which can be functionalized by treatment with organosilanes, such as (3-aminopropyl)trimethoxysilane (see picture).

Mechanistic Studies

M. Uchiyama,* Y. Matsumoto, S. Usui, Y. Hashimoto, K. Morokuma* **926 – 929**

Origin of Chemoselectivity of TMP Zincate Bases and Differences between TMP Zincate and Alkyl Lithium Reagents: A DFT Study on Model Systems

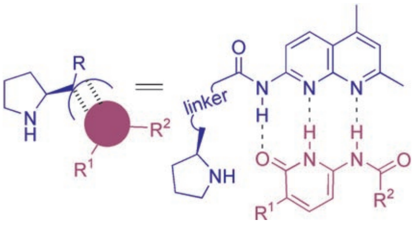


Transition-state structures of the type illustrated were found to be crucial in determining whether directed *ortho*-metalation (DoM) or 1,2-addition occurs in the reaction of benzonitrile or methyl benzoate with $Me_2Zn(TMP)Li$ or $(MeLi)_2$. The origin of the high chemoselectivity of the reaction was investigated. TMP = 2,2,6,6-tetramethylpiperidide.

Homogeneous Catalysis

M. L. Clarke,* J. A. Fuentes **930 – 933**

Self-Assembly of Organocatalysts: Fine-Tuning Organocatalytic Reactions

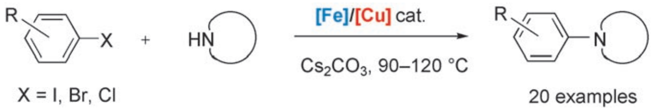


A cat. with two tales: Hydrogen-bonding interactions between achiral pyridinone additives and unselective chiral proline-derived organocatalysts (see picture) result in highly effective catalysts for the Michael addition of nitroalkenes to ketones. In the absence of an additive the reaction is unselective and the product is obtained in about 15 % *ee*, while the same product is obtained with up to 94 % *ee* in the presence of an additive.

C–N Coupling

M. Taillefer,* N. Xia, A. Ouali **934 – 936**

Efficient Iron/Copper Co-Catalyzed Arylation of Nitrogen Nucleophiles

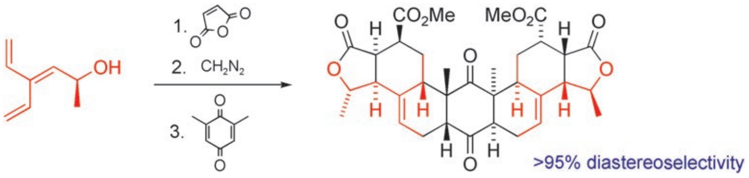


An ideal pair: Various substituted aryl halides react under mild conditions with nitrogen heterocycles in the presence of catalytic amounts of $[Fe(acac)_3]$ (acac = acetylacetonate) and copper salts to give the corresponding cross-coupling products in high yields (see scheme). This cheap and environmentally friendly co-catalyst system is the first example of cooperative Fe/Cu catalysis in this type of N–C bond formation.

Fused-Ring Systems

N. A. Miller, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn* **937 – 940**

Chiral Dendralenes for Rapid Access to Enantiomerically Pure Polycycles

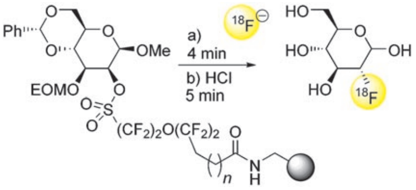


On a short fuse: Highly stereoselective and atom-efficient domino Diels–Alder/lactonization/Diels–Alder sequences can be carried out using simple chiral [3]dendralenes to form fused-ring systems. This short and general approach to cross-conjugated systems promotes the rapid assembly of enantiomerically pure polycyclic ring systems common to biologically interesting terpenoids with virtually complete stereocontrol (see scheme).

Synthetic Methods

L. J. Brown, D. R. Bouvet, S. Champion, A. M. Gibson, Y. Hu, A. Jackson, I. Khan, N. Ma, N. Millot, H. Wadsworth, R. C. D. Brown* ______ **941 – 944**

A Solid-Phase Route to ^{18}F-Labeled Tracers, Exemplified by the Synthesis of [^{18}F]2-Fluoro-2-deoxy-D-glucose

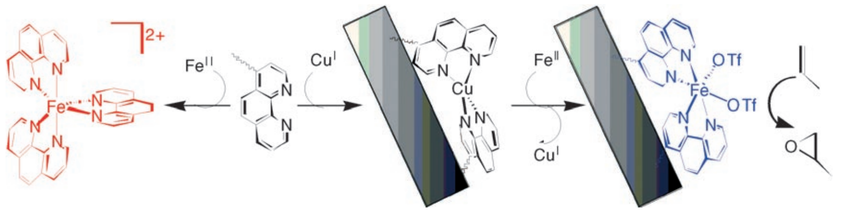


Scintillating synthesis: ^{18}F-Containing radiopharmaceuticals can be prepared by using [^{18}F]fluoride ions to displace a sulfonate linker and release a radiotracer from a solid support (see scheme; EOM = ethoxymethyl). The method has allowed the synthesis of the widely used imaging agent [^{18}F]fluoro-2-deoxy-D-glucose in good radiochemical yield and with high chemical purity.

Heterogeneous Oxidation Catalysis

T. J. Terry, G. Dubois, A. Murphy, T. D. P. Stack* ______ **945 – 947**

Site Isolation and Epoxidation Reactivity of a Templated Ferrous Bis(phenanthroline) Site in Porous Silica

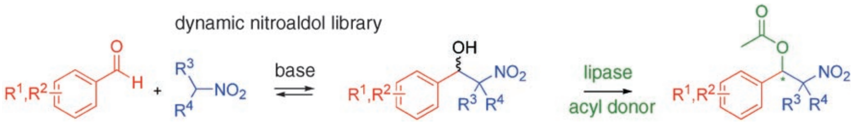


Teaching an old ligand new tricks: Attachment of a Cu^{I}–bis(phenanthroline) complex to mesoporous silica and metal exchange create site-isolated Fe^{II}–bis(phenanthroline) complexes which efficiently epoxidize terminal olefins with peracetic acid (see scheme). This strategy side-steps the formation of a Fe^{II}–tris(phenanthroline) complex, which predominates in solution.

Dynamic Chemistry

P. Vongvilai, M. Angelin, R. Larsson, O. Ramström* ______ **948 – 950**

Dynamic Combinatorial Resolution: Direct Asymmetric Lipase-Mediated Screening of a Dynamic Nitroaldol Library



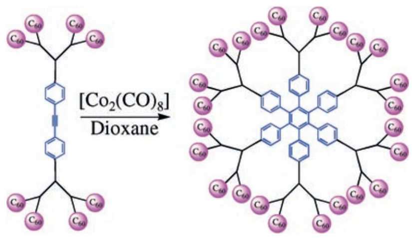
A disturbance in the library: The nitroaldol (Henry) reaction was developed as an efficient C–C bond-forming route to dynamic combinatorial libraries (DCLs). These DCLs generated under thermodynamic control were coupled in a one-pot process with kinetically controlled lipase-mediated transesterification (see scheme). The asymmetric resolution of the DCLs by the enzyme led to enantiomerically pure β-nitroacetates in high yield.

Fullerenes

U. Hahn, E. Maisonhaute, C. Amatore,* J.-F. Nierengarten* ______ **951 – 954**

Synthesis and Electrochemical Properties of Fullerene-Rich Nanoclusters Synthesized by Cobalt-Catalyzed Cyclotrimerization of Bis(aryl)alkyne Fullerodendrimers

A lot of balls: Up to 24 C_{60} units were assembled around a hexaphenylbenzene core by cobalt-catalyzed cyclotrimerization of bis(aryl)alkyne fullerodendrimers (see scheme). Electrochemical investigations reveal that interactions between C_{60} units within a single dendrimer molecule are extremely efficient.

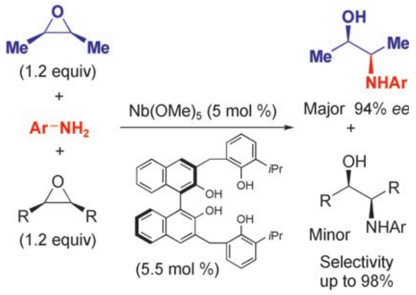


Asymmetric Catalysis

K. Arai, M. M. Salter, Y. Yamashita, S. Kobayashi* ________ **955 – 957**

Enantioselective Desymmetrization of *meso* Epoxides with Anilines Catalyzed by a Niobium Complex of a Chiral Multidentate Binol Derivative

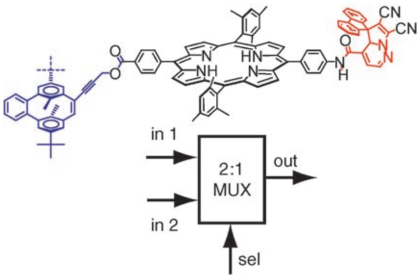
Molecular recognition in the desymmetrization of *meso* epoxides with anilines is displayed by a Lewis acid catalyst formed from niobium(V) methoxide and a novel tetradentate binol derivative. The catalyst has a remarkable ability to distinguish between different *meso* epoxides (see scheme) and also efficiently mediates the ring opening of unsymmetrically disubstituted epoxides with high chemo- and stereoselectivity.



Molecular Electronics

J. Andréasson,* S. D. Straight, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore,* A. L. Moore,* D. Gust* ________ **958 – 961**

Molecular 2:1 Digital Multiplexer



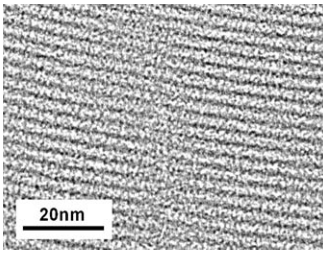
Two into one: A porphyrin linked to two photochromic moieties performs as a 2:1 digital multiplexer (MUX). It takes heat and red light as the two inputs (in 1 and in 2), and a third switchable input (green light, sel) selects whether the output (porphyrin fluorescence) reports the state of in 1 or in 2. Each photochromic moiety may be independently photoisomerized to isomers that quench the porphyrin fluorescence.

Peptide Enrichment

R. Tian, H. Zhang, M. Ye, X. Jiang, L. Hu, X. Li, X. Bao, H. Zou* ________ **962 – 965**

Selective Extraction of Peptides from Human Plasma by Highly Ordered Mesoporous Silica Particles for Peptidome Analysis

Pores for effect: Silica particles with a pore size of 20.5 Å (see TEM image) are effective for enriching peptides in human plasma over a wide range of molecular weights from 1 to 12 kDa, while repelling most other plasma proteins outside. The pore structure of the material makes it superior for peptide enrichment compared to adsorbent- and ultrafiltration-based methods.

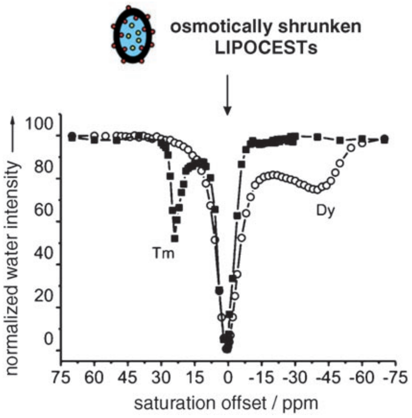


Magnetic Resonance Imaging

E. Terreno, C. Cabella, C. Carrera, D. Delli Castelli, R. Mazzon, S. Rollet, J. Stancanello, M. Visigalli, S. Aime* ________ **966 – 968**

From Spherical to Osmotically Shrunken Paramagnetic Liposomes: An Improved Generation of LIPOCEST MRI Agents with Highly Shifted Water Protons

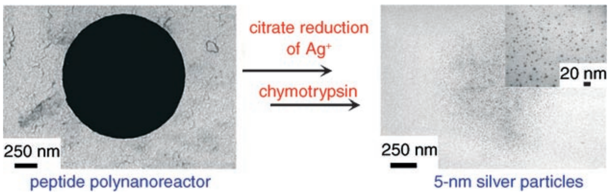
Honey, I shrunk the … The chemical shift of intraliposomal water protons of LIPOCEST MRI agents may be enhanced by exploiting a contribution arising from bulk magnetic susceptibility. The effect was attained by osmotically shrinking liposomes to attain nonspherical compartments, with the largest shifts observed for systems containing paramagnetic Tm or Dy complexes either entrapped in the inner cavity or incorporated in the liposome membrane (see picture).



Nanoreactors

M. G. Ryadnov* ______________ **969 – 972**

A Self-Assembling Peptide Polynanoreactor

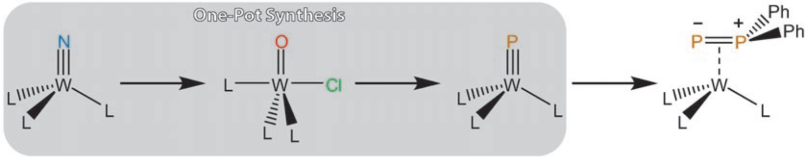


What goes on within: A mesoscopic nanoporous dendrimer-like assembly of peptides hosts numerous nanometer-sized cavities that function as encapsulating sites. As an example, the assembly amplifies a single silver nanoparticle into many discrete nanoparticles of uniform size, and thus it acts as a polynanoreactor (see picture).

Terminal Phosphide Complexes

A. R. Fox, C. R. Clough, N. A. Piro, C. C. Cummins* ______________ **973 – 976**

A Terminal Nitride-to-Phosphide Conversion Sequence Followed by Tungsten Phosphide Functionalization Using a Diphenylphosphenium Synthon

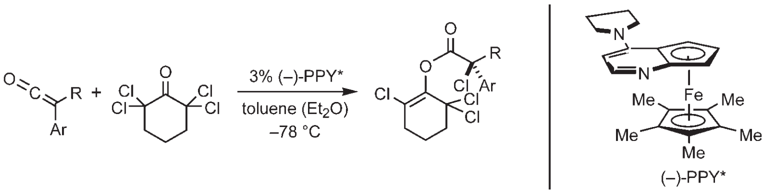


Ligands lost, ligands gained: A terminal tungsten nitride is converted into the corresponding terminal tungsten phosphide by a one-pot sequence of atom-transfer reactions (see scheme). The phosphide complex is subsequently functionalized by treatment with a phosphorus-based electrophile. The resulting phosphorus-rich complex displays P=P multiple-bonding character.

Asymmetric Chlorination

E. C. Lee, K. M. McCauley, G. C. Fu* ______________ **977 – 979**

Catalytic Asymmetric Synthesis of Tertiary Alkyl Chlorides



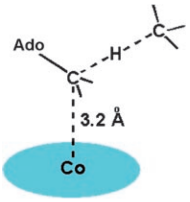
Ketenes are coupled with 2,2,6,6-tetrachlorocyclohexanone in a catalytic asymmetric method for the synthesis of tertiary α-chloroesters (see scheme). This complements recent progress in the generation of secondary α-halocarbonyl compounds.

Enzyme Mechanisms

P. M. Kozlowski,* T. Kamachi, T. Toraya, K. Yoshizawa* ______________ **980 – 983**

Does Cob(II)alamin Act as a Conductor in Coenzyme B_{12} Dependent Mutases?

To conduct a concert of Co–C bond cleavage and subsequent H-atom abstraction may be the role of cob(II)alamin in coenzyme B_{12} dependent mutases (see picture, Ado = adenosyl). Evidence is presented on the basis of DFT analysis that these reactions are concerted and that the radicals generated during the catalytic process are stabilized by the presence of corrin.



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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