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:

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*I. U. Khan, D. Zwanziger, I. Böhme, M. Javed, H. Naseer, S. W. Hyder, A. G. Beck-Sickinger**
Breast Cancer Diagnosis by Neuropeptide Y Analogues: From Synthesis to Clinical Application

S. Yamago, Y. Watanabe, T. Iwamoto*
Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex $[\{Pt(cod)(4,4'\text{-biphenyl})\}_4]$

S. M. Lang, T. M. Bernhardt, R. N. Barnett, U. Landman**
Methane Activation and Catalytic Ethylene Formation on Free Au_2^+

G. Alcaraz, L. Vendier, E. Clot, S. Sabo-Etienne**
Ruthenium Bis(σ-B–H) Aminoborane Complexes from Dehydrogenation of Amine–Boranes: Trapping of $H_2B–NH_2$

K. Meindl, T. Schmiederer, K. Schneider, A. Reicke, D. Butz, S. Keller, H. Gühring, L. Vértesy, J. Wink, H. Hoffmann, M. Brönstrup, G. M. Sheldrick, R. D Süssmuth**
Labyrinthopeptins: A New Class of Carbacyclic Lantibiotics

*K. Suyama, Y. Sakai, K. Matsumoto, B. Saito, T. Katsuki**
Highly Enantioselective Hydrophosphonylation of Aldehydes: Base-Enhanced Aluminum(salalen) Catalysis

*T. Mitsudome, K. Mizumoto, T. Mizugaki, K. Jitsukawa, K. Kaneda**
Wacker-Type Oxidation Using a $PdCl_2$–DMA Catalyst System under Copper-Free Conditions

*A. Pal, M. Bérubé, D. G. Hall**
Design, Synthesis, and Screening of a Library of Peptidyl Bisboroxoles as Low Molecular Weight Receptors for Complex Oligosaccharides in Water: Identification of a Receptor for the Tumor Marker TF-Antigen

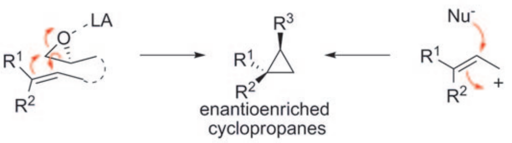
Author Profile

"The secret of being a successful scientist is pertinacity, high frustration tolerance, and ingenuousness. If I could be anyone for a day, I would be Leonardo da Vinci …"
This and more about Christian Limberg can be found on page 484.

Books

Highlights

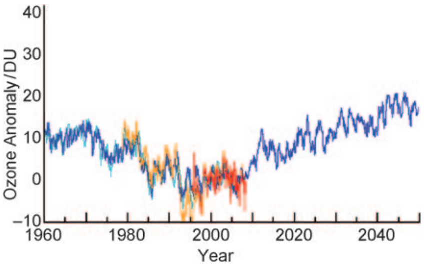
Cyclopropanation



Beating ring strain: Two novel cyclopropanation reactions (see scheme; LA = Lewis acid, Nu = nucleophile) achieved a great level of selectivity using surprisingly mild conditions. The first used epoxides as a source of methylene in the synthesis of enantioenriched cyclopropanes. The second pushed the limit of the well-established allylic alkylation chemistry to the synthesis of three-membered rings with excellent *ee* values.

Contents

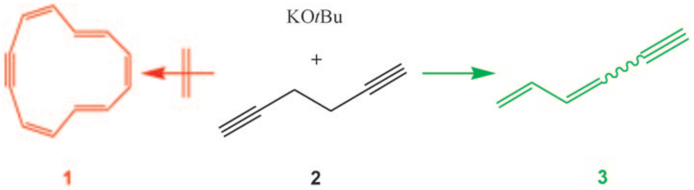
Ozone



Climate change: Atmospheric models predict that climate change will lead to an accelerated recovery of the ozone layer (see plot; orange/red: satellite data, blue: simulations). However, reliable predictions are complicated by the ozone-depleting effect of N_2O. If emissions of this greenhouse gas remain at current levels, by 2050 they could account for 30% of the ozone-destroying effects of chlorofluorocarbons at their peak.

Correspondence

Isomerizations

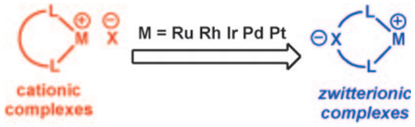


Obscure mechanism: [12]Annulyne **1** and three of its isomers were reported in two recent publications as products from the reaction of potassium *tert*-butoxide (KO*t*Bu) with 1,5-hexadiyne (**2**), although a plausible mechanism was not proposed. A careful examination of the NMR spectra has now proven that only the two possible 1,3-hexadien-5-ynes (**3**) were produced. This result had already been obtained by Sondheimer et al. in 1961.

Reviews

Organometallic Chemistry

Balancing act: Important advances in ancillary ligand design enable the construction of platinum group metal zwitterions. The reactivity of such zwitterions and their more traditionally employed cationic relatives in σ-bond activation chemistry are compared and contrasted.



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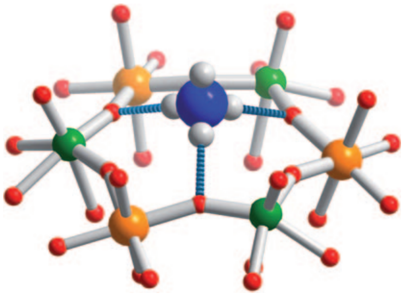
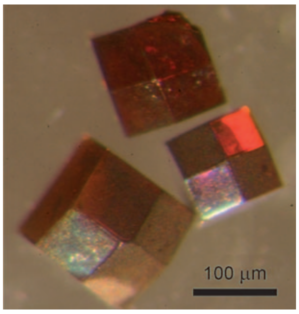
Communications



A manifold of hydrogen-bonding options on a highly active, functionalized capsule surface exhibiting 20 crown ether type pores allows the fixation and recognition of 20 ammonium cations (see picture; W green, Fe orange, O red, N blue, H light gray), which are partially released in solution, thereby leading to related equilibria.

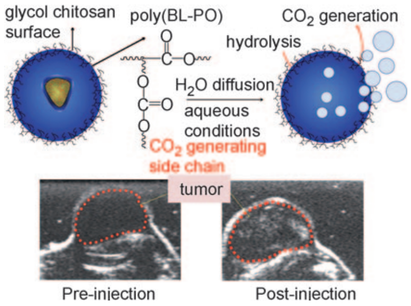
Supramolecular Chemistry



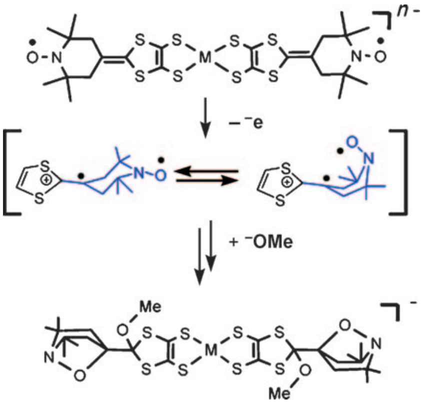
Redox reactions were utilized to deposit periodically arranged Ag and Au nanostructures within the solvent channels of cross-linked lysozyme crystals (see picture for Ag-doped lysozyme crystals). The ability to crystallize lysozyme in various polymorphic forms provides an opportunity to tailor the architecture of the metalized nanostructures through judicious choice of the protein lattice.

Metal Nanostructures

A bubbly personality: Coalescence and fusion of carbon dioxide nanobubbles in a tumor leads to microbubbles that can be imaged by ultrasound (see picture). The bubbles are released from gas-generating polymeric nanoparticles that are coated with hydrophobically modified chitosan. Hydrolysis of the polymer poly(BL-PO), which consists of a biodegradable main backbone and a carbonate side chain, results in the release of carbon dioxide.



Imaging Agents



TEMPO-bound metalladithiolenes, $[M(tempodt)_2]^{n-}$ ($M = Au^{3+}$, $n = 1$; $M = Ni^{2+}$, $n = 2$), show a SOMO–HOMO converted unique electronic structure. The one-electron oxidation of $[M(tempodt)_2]^{n-}$ produces a π radical on the π-conjugated skeleton, which causes an intramolecular cyclization reaction (see picture).

Metalladithiolenes

Frontiers of Chemistry:
From Molecules to Systems

A One-Day Symposium

On 21st May 2010 in Paris

at the Maison de la Chimie
(near the Eiffel Tower and Les Invalides)

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Nobel Prize 2007


Jean-Marie Lehn
Nobel Prize 1987


Roger Y. Tsien
Nobel Prize 2008


Ada Yonath
Nobel Prize 2009


Luisa De Cola


Alan R. Fersht


Marc Fontecave


Michael Grätzel


Michel Orrit


Nicolas Winssinger

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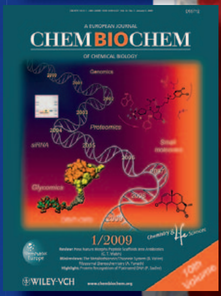

Scientific committee

E. Amouyal, M. Che,
F. C. De Schryver,
A. R. Fersht, P. Gölitz,
J. T. Hynes, J.-M. Lehn

Topics

catalysis, biochemical imaging, chemical biology, bionanotechnology, proteomics, spectroscopy, solar cells

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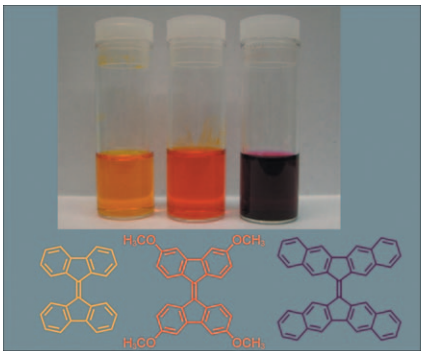
530320908

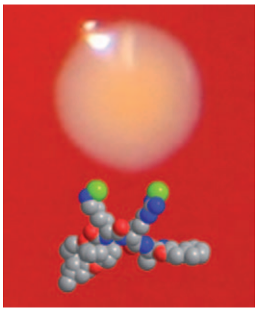
Straining at the leash: The main features of electron-accepting materials with a 9,9′-bifluorenylidene backbone are strain relief and a gain in aromaticity. These dimers (see picture) exhibit absorption near the red spectral region (ca. 600 nm) and HOMO (5.58–5.06 eV) and LUMO (3.37–3.09 eV) energy levels, which, together with high solubility and thermal stability render these materials attractive acceptors for bulk heterojunction (BHJ) solar cells.



Organic Electronics

F. G. Brunetti, X. Gong, M. Tong,
A. J. Heeger, F. Wudl* ________ **532 – 536**

Strain and Hückel Aromaticity: Driving Forces for a Promising New Generation of Electron Acceptors in Organic Electronics



Superbugs stalled! Two newly designed synthetic dicationic peptoids (see one example; red O, blue N, green Cl) show promising in vitro bactericidal activity against a range of Gram-positive pathogens, including organisms resistant to vancomycin, methicillin, and linezolid, with only slow development of resistance. Moreover their potency is maintained in vivo.

Antibiotics

J. B. Bremner,* P. A. Keller,* S. G. Pyne,*
T. P. Boyle, Z. Brkic, D. M. David, A. Garas,
J. Morgan, M. Robertson, K. Somphol,
M. H. Miller, A. S. Howe, P. Ambrose,
S. Bhavnani, T. R. Fritsche,
D. J. Biedenbach, R. N. Jones,
R. W. Buckheit, Jr., K. M. Watson,
D. Baylis, J. A. Coates, J. Deadman,
D. Jeevarajah, A. McCracken,
D. I. Rhodes ________ **537 – 540**

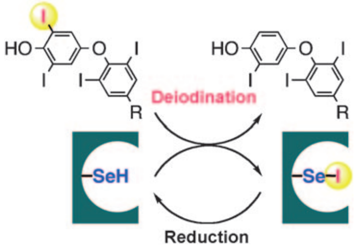
Binaphthyl-Based Dicationic Peptoids with Therapeutic Potential

Whitewater RAFTing: High-molecular-weight (HMW) (co)polymers can be formed using ARGET ATRP with alkyl pseudohalides as initiators and chain-transfer agents. This system works with parts-per-million quantities of copper(I) catalyst whilst retaining excellent control over molecular weight, molecular weight distribution, and chain-end functionality. Copper wire (see picture) can be used as reducing agent several times without additional treatment.

Radical Polymerization

R. Nicolaÿ, Y. Kwak,
K. Matyjaszewski* ________ **541 – 544**

A Green Route to Well-Defined High-Molecular-Weight (Co)polymers Using ARGET ATRP with Alkyl Pseudohalides and Copper Catalysis



What makes a good cavity? A molecular cavity enabled the stabilization of a selenenyl iodide (RSeI) intermediate formed in 5′-deiodination of a thyroxine derivative by an organoselenol (see scheme). The chemical processes proposed for the iodothyronine deiodinase catalytic cycle were experimentally established.

Enzyme Models

K. Goto,* D. Sonoda, K. Shimada, S. Sase,
T. Kawashima* ________ **545 – 547**

Modeling of the 5′-Deiodination of Thyroxine by Iodothyronine Deiodinase: Chemical Corroboration of a Selenenyl Iodide Intermediate

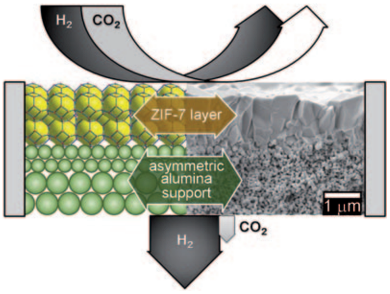
Contents

Microporous Membranes

Y.-S. Li,* F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang, J. Caro* ________ **548 – 551**

Molecular Sieve Membrane: Supported Metal–Organic Framework with High Hydrogen Selectivity

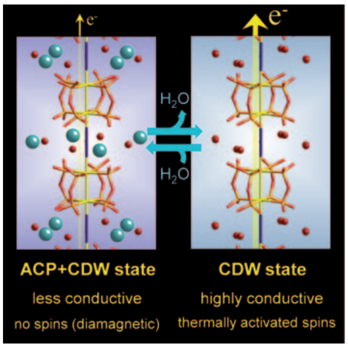
Molecular strainer: An ultramicroporous zeolitic imidazolate framework (ZIF-7) was tested for its gas-separation properties in membrane applications. ZIF-7 was appended to an asymmetric alumina support using microwave-assisted seeded growth, and the resulting ZIF-7 membrane exhibits high H_2 selectivity as a molecular sieve and has excellent thermal stability.



Vapor-Induced Switching

H. Iguchi, S. Takaishi, H. Miyasaka, M. Yamashita,* H. Matsuzaki, H. Okamoto, H. Tanaka, S.-i. Kuroda ________ **552 – 555**

Water-Vapor-Induced Reversible Switching of Electronic States in an MMX-Type Chain Complex with Retention of Single Crystallinity



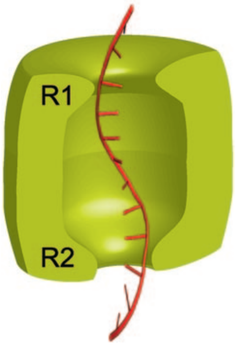
Back and forth: Reversible structural change and changes in the physical properties of a quasi-1D dinuclear Pt complex occurred with dehydration and rehydration. Upon dehydration, the electronic state changed from an alternating charge-polarization and charge-density-wave (ACP+CDW) state to a narrow-gapped CDW state with an increase in the electrical conductivity and molar spin susceptibility at room temperature.

DNA Sequencing

D. Stoddart, G. Maglia, E. Mikhailova, A. J. Heron, H. Bayley* ______ **556 – 559**

Multiple Base-Recognition Sites in a Biological Nanopore: Two Heads are Better than One

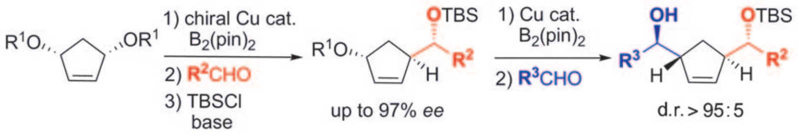
The α-hemolysin nanopore is a promising sensor for ultra-rapid sequencing of DNA strands within nanopores. By using immobilized synthetic oligonucleotides, it is shown that additional sequence information can be gained when two recognition sites, rather than one, are employed within a single nanopore (see picture).



Desymmetrization

H. Ito,* T. Okura, K. Matsuura, M. Sawamura ________ **560 – 563**

Desymmetrization of *meso*-2-Alkene-1,4-diol Derivatives through Copper(I)-Catalyzed Asymmetric Boryl Substitution and Stereoselective Allylation of Aldehydes

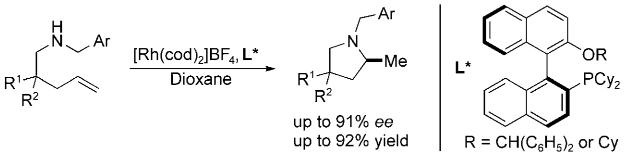


Breaking the mirror: The reaction sequence described in the title was applied to the synthesis of a valuable chiral drug precursor and the rapid stereoselective assembly of complex compounds with multiple chiral centers (see scheme).

Asymmetric Catalysis

X. Shen, S. L. Buchwald* ______ 564–567

Rhodium-Catalyzed Asymmetric Intramolecular Hydroamination of Unactivated Alkenes

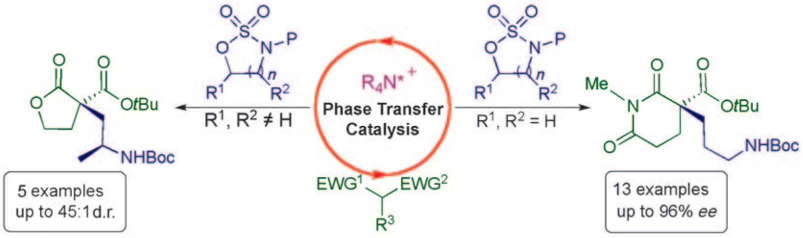


One for the Rh(oad): The first rhodium-catalyzed asymmetric intramolecular hydroamination of unactivated olefins was developed by using dialkylbiaryl phosphine ligands (see scheme; cod = 1,5-cyclooctadiene, Cy = cyclohexyl). A variety of 2-methylpyrrolidines have been synthesized with high enantioselectivities.

Phase-Transfer Catalysis

T. A. Moss, B. Alonso, D. R. Fenwick, D. J. Dixon* ______ 568–571

Catalytic Enantio- and Diastereoselective Alkylations with Cyclic Sulfamidates

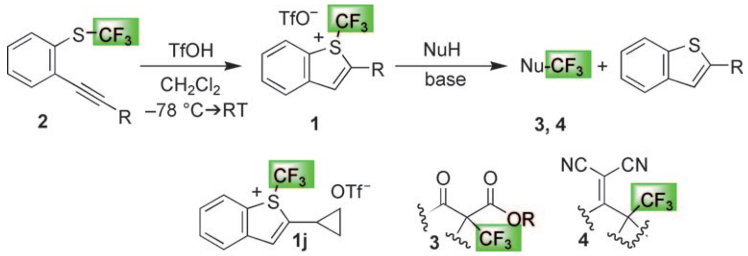


Open for business: The enantio- and diastereoselective nucleophilic ring opening of five-membered and six-membered cyclic sulfamidates under asymmetric phase-transfer catalysis is presented. A range of pro-nucleophiles have been successfully alkylated in good yields and in good to excellent enantioselectivites.

C–C Bond Formation

A. Matsnev, S. Noritake, Y. Nomura, E. Tokunaga, S. Nakamura, N. Shibata* ______ 572–576

Efficient Access to Extended Yagupolskii–Umemoto-Type Reagents: Triflic Acid Catalyzed Intramolecular Cyclization of *ortho*-Ethynylaryltrifluoromethylsulfanes

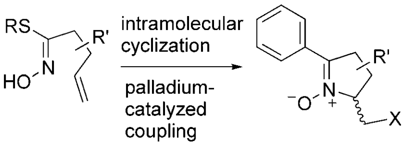


King of the ring: *S*-(trifluoromethyl)benzo[b]thiophenium salts **1**, as analogues of Yagupolskii–Umemoto type reagents, were synthesized by novel triflic acid catalyzed intramolecular cyclization of *ortho*-ethynylaryltrifluoromethylsulfanes **2**. **1j** is especially useful for the electrophilic trifluoromethylation of β-ketoesters and dicyanoalkylidenes.

Coupling Reactions

J. Schleiss, P. Rollin, A. Tatibouët* ______ 577–580

Palladium-Catalyzed Coupling Reactions of Thioimidate N-Oxides: Access to α-Alkenyl- and α-Aryl-Functionalized Cyclic Nitrones



Surprisingly useful are thioimidate N-oxides in the preparation of aryl- and vinyl-substituted cyclic ketonitrones through the Liebeskind–Srogl reaction. This novel synthetic approach appears to be efficient and have a broad scope (see scheme).

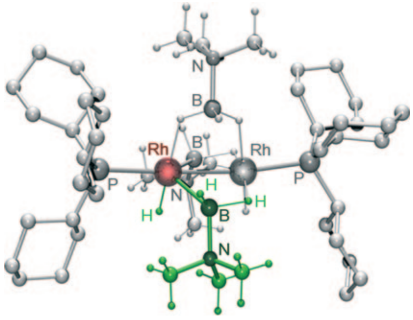
Contents

Amine–Boranes

A. B. Chaplin, A. S. Weller* ___ **581 – 584**

B–H Activation at a Rhodium(I) Center: Isolation of a Bimetallic Complex Relevant to the Transition-Metal-Catalyzed Dehydrocoupling of Amine–Boranes

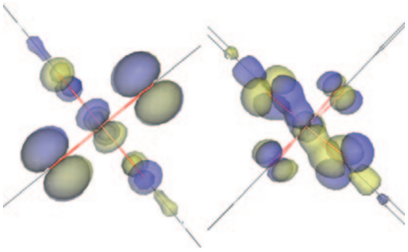
The missing link: A bimetallic complex that is relevant to the mechanism of transition-metal-catalyzed amine–borane dehydrocoupling has been isolated. The structure (see picture) contains three different amine–borane activation modes within the same molecule.



Metal–Organic Frameworks

V. K. Peterson,* G. J. Kearley, Y. Wu, A. J. Ramirez-Cuesta, E. Kemner, C. J. Kepert ___ **585 – 588**

Local Vibrational Mechanism for Negative Thermal Expansion: A Combined Neutron Scattering and First-Principles Study

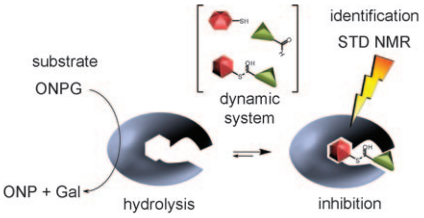


Ask the locals: Dynamic deformation of the dicopper tetracarboxylate paddlewheel unit within a metal–organic framework from square-prismatic (see picture, left) to distorted (right) occurs at very low energies. This deformation, which contributes strongly to the negative thermal expansion of this system, is a local vibration induced by a redistribution of electron density at the Cu–O junctions.

Dynamic Chemistry

R. Caraballo, H. Dong, J. P. Ribeiro, J. Jiménez-Barbero, O. Ramström* ___ **589 – 593**

Direct STD NMR Identification of β-Galactosidase Inhibitors from a Virtual Dynamic Hemithioacetal System

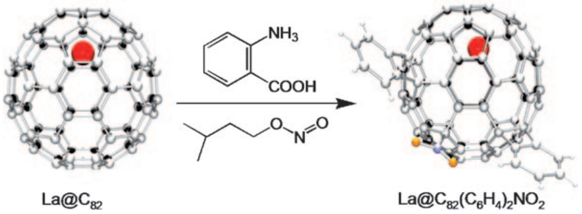


Resolving complex systems: The formation of a dynamic hemithioacetal system and its application toward the discovery of β-galactosidase inhibitors were successfully investigated. The designed dynamic system, which has a virtual character in neutral aqueous media, was subjected to a direct in situ identification of the best inhibitors by ^{1}H STD NMR spectroscopy (ONPG: *o*-nitrophenyl-β-galactopyranoside).

Fullerenes

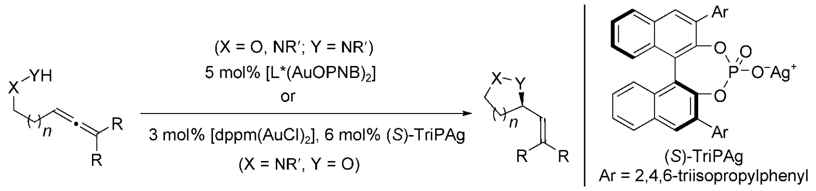
X. Lu, H. Nikawa, T. Tsuchiya, T. Akasaka,* M. Toki, H. Sawa, N. Mizorogi, S. Nagase* ___ **594 – 597**

Nitrated Benzyne Derivatives of La@C$_{82}$: Addition of NO$_2$ and Its Positional Directing Effect on the Subsequent Addition of Benzynes



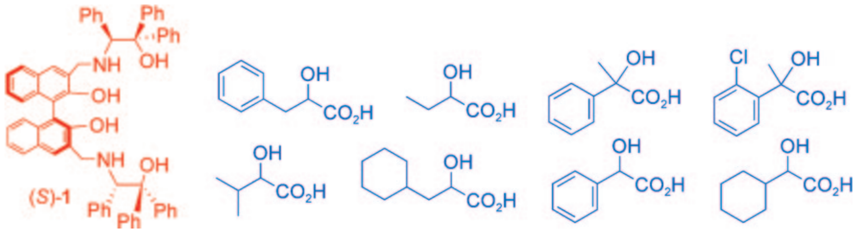
Dragon Ball La: The unprecedented addition of NO$_2$ and two benzene moieties to metallofullerene La@C$_{82}$ is described. The X-ray structure (see picture, right) shows an NO$_2$ group that is singly bound to a cage carbon that has a high degree of radical character, and two benzene moieties that are linked to highly pyramidalized cage carbon atoms through [5,6]-bond junctions.

Gold Catalysis



Au-ff on a trip: Chiral ligands (L*) and chiral anions [(S)-TriPAg] are employed in the gold(I)-catalyzed enantioselective intramolecular additions of hydrazines and hydroxylamines to allenes. These complementary methods allow access to chiral vinyl isoxazolidines, oxazines, and differentially protected pyrazolidines. PNB = *para*-nitrobenzoyl.

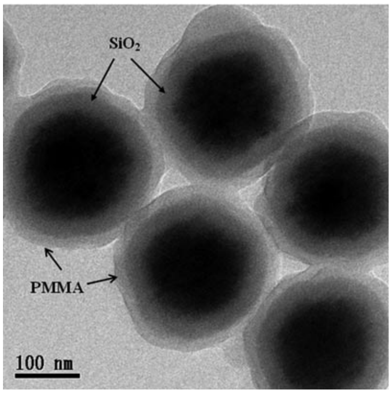
Fluorescent Sensors



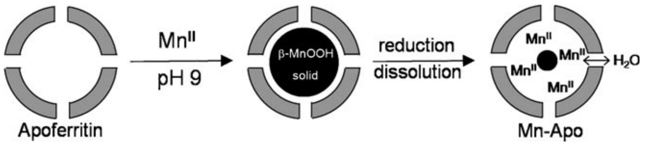
The shining: Readily accessible BINOL amino alcohol (*S*)-**1** is a highly enantioselective fluorescent sensor for structurally diverse α-hydroxycarboxylic acids, and is the first highly enantioselective fluorescent sensor for the recognition of linear aliphatic α-hydroxycarboxylic acids and α-tertiary-hydroxycarboxylic acids.

Microparticles

Particularly enriching: Core–shell–shell $Fe_3O_4@SiO_2@PMMA$ composite microspheres (see picture; PMMA = poly(methyl methacrylate)) were synthesized readily by combining a sol-gel approach with a seeded aqueous-phase radical polymerization method. The microspheres were successfully applied toward the effective, rapid, and convenient enrichment of low-concentration peptides and proteins for mass spectrometric analysis.



MRI Contrast Agents

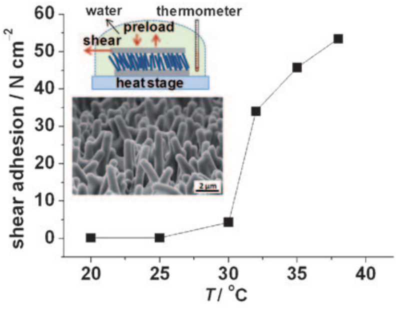


A manganese-based contrast agent for magnetic resonance imaging has been obtained by partial reduction/dissolution of solid β-MnOOH inside the cavity of apoferritin (see scheme). The resulting nanocarriers contain up to 300–400 Mn^{II} aqua ions and have a remarkable relaxivity of 4000–7000 $mM^{-1}s^{-1}$ per apoferritin unit.

Nanowires

H. Ko, Z. Zhang, Y.-L. Chueh, E. Saiz, A. Javey* ________ **616 – 619**

Thermoresponsive Chemical Connectors Based on Hybrid Nanowire Forests



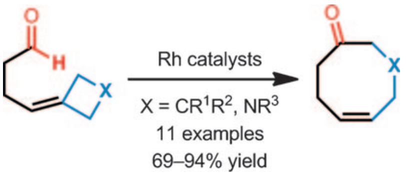
Sticking around in the heat: Self-selective, programmable fasteners, based on hybrid core/multishell nanowire forests with an outer shell of poly(*N*-isopropylacrylamide) hydrogel, reversibly change their wet adhesion properties in response to a change in temperature. The shear adhesion strength of the nanowire fasteners can be modulated by a factor of 170 in under 5 min in response to a temperature change of 5 °C.

C–H Activation

D. Crépin, J. Dawick, C. Aïssa* **620 – 623**

Combined Rhodium-Catalyzed Carbon–Hydrogen Activation and β-Carbon Elimination to access Eight-Membered Rings

Enlarge! C–H bond activation and β-carbon elimination are combined in a net intramolecular hydroacylation of alkylidenecyclobutanes and alkylideneazetidines in the presence of rhodium catalysts, affording eight-membered-ring compounds in high yield (see scheme). This study demonstrates the possibility of exploiting the strain energy of azetidines through β-carbon elimination in new transition-metal-catalyzed reactions.

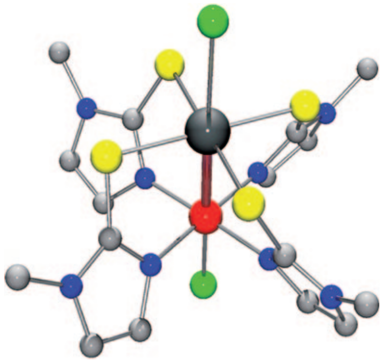


Transition-Metal–Silicon Bonds

J. Wagler,* E. Brendler ________ **624 – 627**

Metallasilatranes: Palladium(II) and Platinum(II) as Lone-Pair Donors to Silicon(IV)

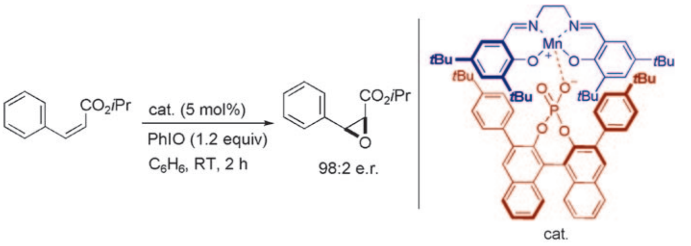
Caught by the octopus: The first structurally characterized metallasilatranes exhibit strong, formally dative Pd→Si and Pt→Si bonds (see picture; C gray, N blue, Si red, S yellow, Cl green, Pt black). The Si atoms are hexacoordinate, and the transition-metal (TM) atom is a lone-pair donor. Short TM–Si separations, pronounced upfield ^{29}Si NMR signals, and strong Si–Pt coupling show the interaction between the TM atom and a main-group element with an octet shell.



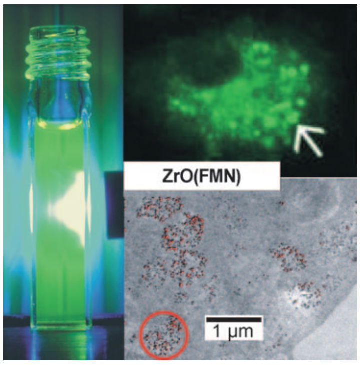
Asymmetric Epoxidation

S. Liao, B. List* ________ **628 – 631**

Asymmetric Counteranion-Directed Transition-Metal Catalysis: Enantioselective Epoxidation of Alkenes with Manganese(III) Salen Phosphate Complexes



Paired up: A highly active and enantioselective ion-pair epoxidation catalyst, consisting of an achiral Mn^{III}–salen complex and a chiral phosphate counteranion, mediates the epoxidization of a wide range of alkenes with high yields and enantioselectivities (see scheme). The unique role of the counteranion is to stabilize an enantiomorphic conformation of the cationic Mn catalyst.



Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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