



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:

C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh,* A. Müller*

Unprecedented and Differently Applicable Pentagonal Units in a Dynamic Library: A Keplerate of the Type $\{(W)W_5\}_{12}\{Mo_2\}_{30}$

S. W. Hong, M. Byun, Z. Lin*

Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids

L. Catala,* D. Brinzei, Y. Prado, A. Gloter, O. Stéphan, G. Rogez, T. Mallah*

Core–Multishell Magnetic Coordination Nanoparticles: Towards Multifunctionality at the Nanoscale

D. Morton, S. Leach, C. Cordier, S. Warriner, A. Nelson*

Synthesis of Natural-Product-Like Molecules with Over Eighty Distinct Scaffolds

P. Hazarika, S. M. Jickells, K. Wolff, D. A. Russell*

Imaging of Latent Fingerprints through the Detection of Drugs and Metabolites

O. Vendrell, F. Gatti, H.-D. Meyer*

Strong Isotope Effects in the Infrared Spectrum of the Zundel Cation

W. M. Czaplik, M. Mayer, A. J. van Wangelin*

Domino Iron Catalysis: Direct Aryl–Alkyl Cross-Coupling

Nitroxides

Gertz L. Likhtenshtein, Jun Yamauchi, Shin'ichi Nakatsuji, Alex I. Smirnov, Rui Tamura

Organic Chemistry:

S. E. Denmark Honored _____ 9598

Asymmetric Catalysis:

M. Shibasaki Awarded _____ 9598

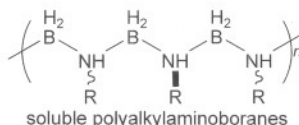
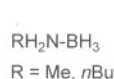
Books

reviewed by N. J. Turro, J. Y.-C. Chen 9596

News

Inorganic Chemistry:

Prizes for D. Scheschkewitz _____ 9598



Taking the high road is what reactions of primary amine boranes do, according to results recently obtained by Manners and co-workers, when a homogeneous catalyst is used to prepare soluble aminoborane polymers and copolymers (see scheme;

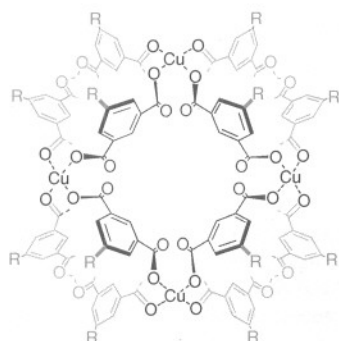
pocop = κ^3 -1,3-($OPtBu_2$)₂C₆H₃). Such metal-catalyzed dehydrocoupling reactions for the synthesis of new B–N analogues of α -olefins are of fundamental interest for materials science.

Highlights

Soluble B–N Polymers

V. Pons, R. T. Baker* _____ 9600–9602

Soluble Boron–Nitrogen High Polymers from Metal-Complex-Catalyzed Amine Borane Dehydrogenation



Space—the final frontier: Recent progress with metal–organic scaffolds (see picture for an example) to create synthetic ion channels and pores is summarized in this Highlight. The great advantage of this approach is access to a stable and large confined space from small structural units. Current breakthroughs promise future progress toward the synthesis of tubular structures and their multiple functionalization.

Supramolecular Chemistry

N. Sakai, S. Matile* _____ 9603–9607

Metal–Organic Scaffolds: Heavy-Metal Approaches to Synthetic Ion Channels and Pores

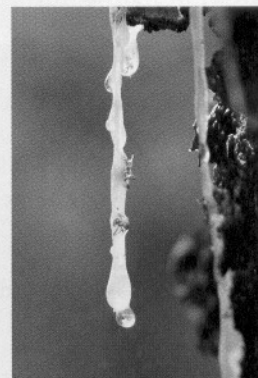
Minireviews

Amber

J. B. Lambert,* J. A. Santiago-Blay,*
K. B. Anderson* ————— 9608–9616

Chemical Signatures of Fossilized Resins
and Recent Plant Exudates

The chemical fingerprint of amber may be detected in terms of molecular components by pyrolysis GC–MS or in terms of ^{13}C NMR resonances. Understanding the components of amber can permit association with geographical and botanical sources. The picture shows an exudate with entrapped ants from a pine tree in the U.S. National Arboretum, Washington, DC. (Photograph by Chip Clark, National Museum of Natural History, Washington, DC).



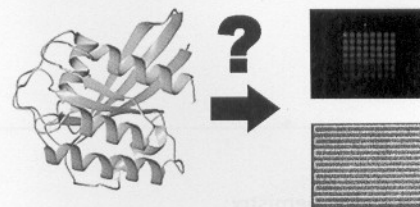
Reviews

Protein Biochips

P. Jonkheijm, D. Weinrich, H. Schröder,
C. M. Niemeyer,*
H. Waldmann* ————— 9618–9647

Chemical Strategies for Generating
Protein Biochips

Putting the protein on the chip: This Review discusses chemical strategies, both covalent and noncovalent, for attaching proteins to surfaces to make protein biochips. Particular emphasis is put on the chemical specificity of protein attachment and on retention of protein function. Strategies for creating protein patterns (as opposed to protein arrays) are also presented.

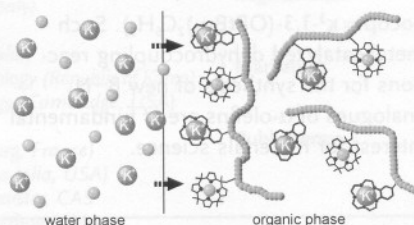


Communications

Polymeric Extractants

A. Aydogan, D. J. Coady, S. K. Kim,
A. Akar,* C. W. Bielawski,* M. Marquez,
J. L. Sessler* ————— 9648–9652

Poly(methyl methacrylate)s with Pendant
Calixpyrroles and Crown Ethers: Polymeric
Extractants for Potassium Halides



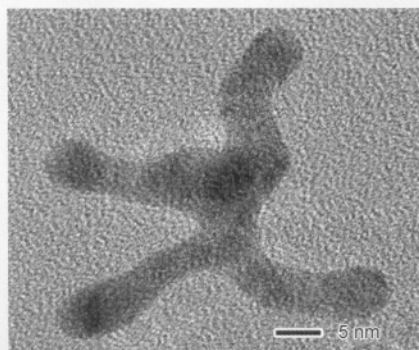
Fishing for KF: Potassium fluoride and chloride salts can be extracted from aqueous media using poly(methyl methacrylate)s containing pendant calix[4]pyrrole and crown ether groups (see picture). These polymers are able to extract these salts much more efficiently than calixpyrrole, crown ether, linked crown ether calixpyrrole monomers, polymers containing either recognition unit, or poly(methyl methacrylate) controls.

For the USA and Canada:

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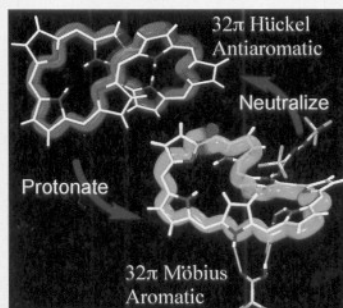
Self-destruct mechanism: Gold multipods are formed by a galvanic replacement reaction of AuCl with a self-destructive template consisting of a three-dimensional aggregate of magnetic iron nanoparticles. As a unique feature of this system, the template spontaneously falls apart during the reaction to automatically release the resultant gold multipods.

Gold Nanostructures

Z. Li, W. Li, P. H. C. Camargo, Y. Xia* 9653–9656

Facile Synthesis of Branched Au Nanostructures by Templating Against a Self-Destructive Lattice of Magnetic Fe Nanoparticles

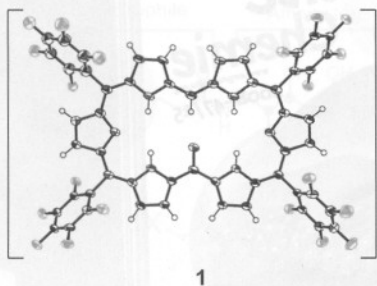
Switching Aromaticity: Conformations of [32]heptaphyrins (1.1.1.1.1.1.1) are dependent upon meso-aryl substituents, solvents, temperature, and protonation. Particularly, protonation of meso-pentafluorophenyl-substituted [32]heptaphyrin triggers conformational changes to form twisted aromatic Möbius structures (see picture), even at room temperature.



Aromaticity

S. Saito, J.-Y. Shin, J. M. Lim, K. S. Kim, D. Kim,* A. Osuka* 9657–9660

Protonation-Triggered Conformational Changes to Möbius Aromatic [32]Heptaphyrins (1.1.1.1.1.1.1)



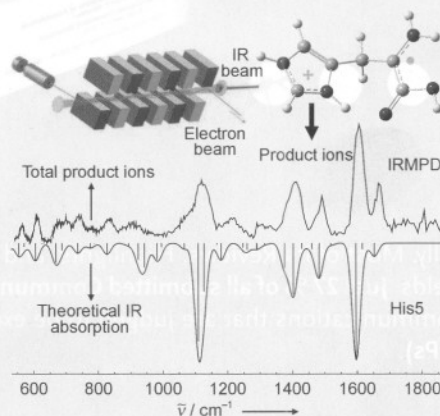
A stable radical: The title compound **1** has been synthesized as the first example of a meso-free variant and characterized as a strongly aromatic macrocycle with a spectacles-like planar conformation. The incorporation of free meso positions is promising for the exploration of novel structural and electronic properties.

Porphyrinoids

T. Koide, G. Kashiwazaki, M. Suzuki, K. Furukawa, M.-C. Yoon, S. Cho, D. Kim,* A. Osuka* 9661–9665

A Stable Radical Species from Facile Oxygenation of meso-Free 5,10,20,25-Tetrakis(pentafluorophenyl)-Substituted [26]Hexaphyrin (1.1.1.1.1.1)

The observable histidine radical cation generated by collision-induced dissociation of the [Cu^{II}(2,2':6',2''-terpyridine)-(His)]²⁺ complex carries the positive charge on the protonated imidazole ring and the radical formally on the α carbon. This structure has been confirmed by infrared multiple photon dissociation (IRMPD) spectroscopy and density functional calculations.

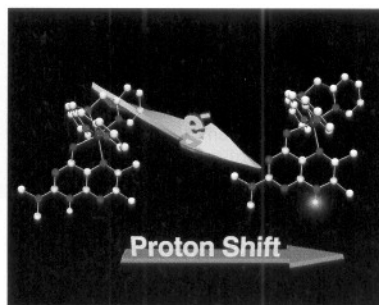


Radical Cations

J. Steill, J. Zhao, C.-K. Siu, Y. Ke, U. H. Verkerk, J. Oomens, R. C. Dunbar, A. C. Hopkinson, K. W. M. Siu* 9666–9668

Structure of the Observable Histidine Radical Cation in the Gas Phase: A Captodative α -Radical Ion

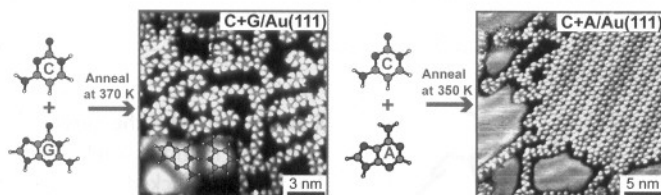
A shift in focus: Fully oxidized pterins coordinated to ruthenium(II) undergo a first protonation at the nitrogen atom at the 1-position of the pyrimidinone moiety. Subsequent one-electron reduction induces an unprecedented proton shift from the nitrogen atom at the 1-position to that at the 8-position of the pyrazine moiety (see picture; C white, H yellow, N blue, O red).



Metal–Coenzyme Complexes

S. Miyazaki, K. Ohkubo, T. Kojima,*
S. Fukuzumi* 9669–9672

Proton Shift upon One-Electron
Reduction in Ruthenium(II)-Coordinated
Pterins



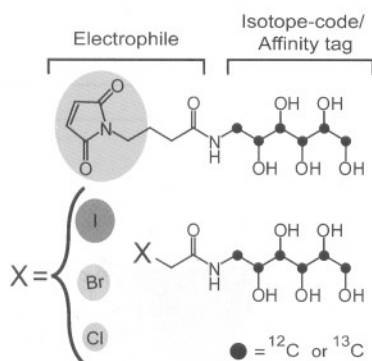
Surface Watson–Crick base pairing makes binary mixtures of the complementary nucleobases guanine (G) and cytosine (C) on Au(111) thermally stable up to the desorption temperature of the bases,

whereas binary mixtures of the noncomplementary adenine (A) and cytosine segregate on heating (see STM images with DFT structures).

Surface Nucleobase Pairing

R. Otero, W. Xu, M. Lukas, R. E. A. Kelly,
E. Lægsgaard, I. Stensgaard, J. Kjems,
L. N. Kantorovich,
F. Besenbacher* 9673–9676

Specificity of Watson–Crick Base Pairing
on a Solid Surface Studied at the Atomic
Scale



Another foot forward: Isotope-coded affinity tag (ICAT) reagents are versatile probes for footprinting dynamic protein structure. To render ICAT footprinting effective, a series of ICAT reagents with alkylation rates that span five orders of magnitude was designed. With this toolkit, an unprecedented range of Cys residues can be footprinted, including those deeply buried in the protein core and those involved in protein–protein interactions of modest affinity.

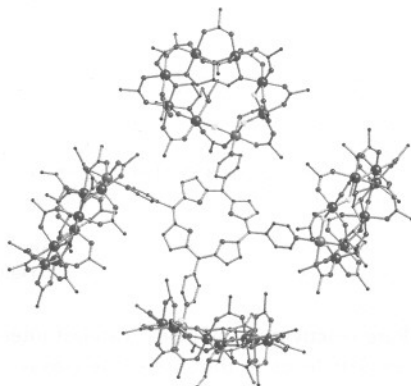
Protein Dynamics

E. S. Underbakke, Y. Zhu,
L. L. Kiessling* 9677–9680

Isotope-Coded Affinity Tags with Tunable
Reactivities for Protein Footprinting



Sugared donuts: Reactions of hydrated chromium fluoride with *N*-ethyl-D-glucamine (H_5Etglu) in pivalic acid, in the presence of nickel carbonate, leads to heterometallic “glu-ed” rings. These rings allow for construction of polyring arrays, for example an assembly where four glu-ed rings are attached to tetrapyrrolylporphyrin (see structure; F yellow, O red, N blue, Cr purple, Ni green, C black).



Metallocycles

G. A. Timco,* E. J. L. McInnes,
R. G. Pritchard, F. Tuna,
R. E. P. Winpenny* 9681–9684

Heterometallic Rings Made From
Chromium Stick Together Easily

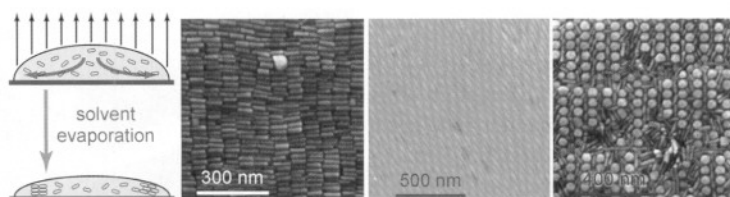


Ordered Assemblies

T. Ming, X. S. Kou, H. J. Chen, T. Wang,
H.-L. Tam, K.-W. Cheah, J.-Y. Chen,*
J. F. Wang* 9685–9690



Ordered Gold Nanostructure Assemblies
Formed By Droplet Evaporation



The order of gold: Ordered assemblies of gold nanostructures are produced by droplet evaporation from single- and two-component systems. The ordering of the assemblies is highly dependent on the shape and size of gold nanostructures and

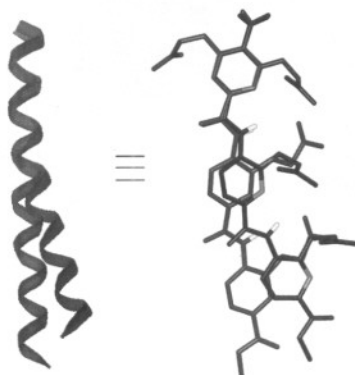
includes nanorods, nanocubes, polyhedra, and bipyramids. The two-photon-excited luminescence of ordered gold nanorod assemblies is larger than that of disordered nanorod assemblies.

α -Helix Mimetics

I. Saraogi, C. D. Incarvito,
A. D. Hamilton* 9691–9694



Controlling Curvature in a Family of
Oligoamide α -Helix Mimetics



Catching up with the curve! The natural curvature found in a majority of α helices has been mimicked in small synthetic oligoamide scaffolds. Differences in hydrogen-bonding patterns in these scaffolds lead to mimetics with varying degrees of curvature in the backbone. This adds another parameter to the structural and functional mimicry of α helices.

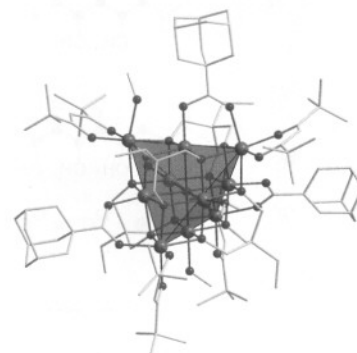
Cluster Compounds

L. Lisnard, F. Tuna, A. Candini,
M. Affronte, R. E. P. Winpenny,
E. J. L. McNnes* 9695–9699



Supertetrahedral and Bi-supertetrahedral
Cages: Synthesis, Structures, and
Magnetic Properties of Deca- and
Enneadecametallic Cobalt(II) Clusters

Magnetic cage: Simple cobalt(II) diketonates react with triols under solvothermal conditions to give a family of compounds based on supertetrahedral cage structures: a regular and a distorted $\{\text{Co}^{\text{II}}_{10}\}$ species, and a bi-supertetrahedral $\{\text{Co}^{\text{II}}_{19}\}$ species. Magnetic studies show unusual properties, such as nonvanishing magnetization below 12 K, which until now have only been detected in a family of $\{\text{Ni}_{10}\}$ clusters.

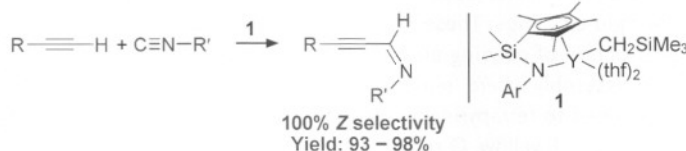


Homogeneous Catalysis

W.-X. Zhang, M. Nishiura,
Z. Hou* 9700–9703



Synthesis of (Z)-1-Aza-1,3-enynes by the
Cross-Coupling of Terminal Alkynes with
Isocyanides Catalyzed by Rare-Earth Metal
Complexes



Rare reactivity: A binuclear catalyst intermediate leads to the Z-selective cross-coupling of terminal alkynes with isocya-

nides to exclusively yield the (Z)-1-aza-1,3-enyne products for the first time (see scheme).



Cold guests lower the tone: The thermally induced phase transition in the hexagonal clathrate hydrate containing cyclooctane is reversible. This transition is most likely related to the freezing-in of the motion of the low-symmetry cyclooctane guest (see picture: colors indicate different orientations of the guest and associated distortions of the host).

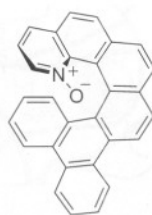
Clathrate Structures

K. A. Udachin, C. I. Ratcliffe,
G. D. Enright,
J. A. Ripmeester* — 9704–9707

Transformation of the Hexagonal-
Structure Clathrate Hydrate of
Cyclooctane to a Low-Symmetry Form
Below 167 K



up to 94% ee



(*P*)-1-azahelicene *N*-oxide
1

Asymmetric Catalysis

N. Takenaka,* R. S. Sarangthem,
B. Captain — 9708–9710

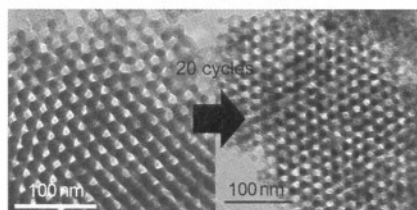
Helical Chiral Pyridine *N*-Oxides: A New
Family of Asymmetric Catalysts



Helical Chiral Catalysts: The gram-scale synthesis of 1-azahelicenes, structural characterization of the corresponding *N*-oxides, and the application of this new family of catalysts to the catalytic, enantioselective ring-opening of *meso* epoxides

is described (see scheme). Included is the first demonstration that the appropriate structural modifications beneath the plane of the pyridine *N*-oxide can serve as a powerful means for tuning the catalyst enantioselectivity.

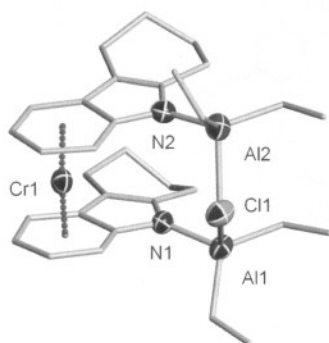
Sturdy spinel: A mesoporous Li–Mn–O spinel ($\text{Li}_{1.12}\text{Mn}_{1.88}\text{O}_4$) with superior rate capability at ambient temperature is synthesized. Comparable stability to the bulk material at elevated temperatures is also observed, despite a surface area of $90\text{ m}^2\text{ g}^{-1}$ for the mesopore, suggesting that the internal mesopore surfaces are more stable than the external surface.



Mesoporous Cathodes

F. Jiao, J. Bao, A. H. Hill,
P. G. Bruce* — 9711–9716

Synthesis of Ordered Mesoporous
Li–Mn–O Spinel as a Positive Electrode
for Rechargeable Lithium Batteries



One more trimer: A series of chromium complexes of different oxidation states are employed as catalysts for the polymerization/oligomerization of ethylene. The results suggest a link between chromium oxidation state and catalytic performance, with Cr^{III} leading to oligomerization, Cr^{II} to polymerization, and Cr^{I} to selective trimerization.

Catalyst Design

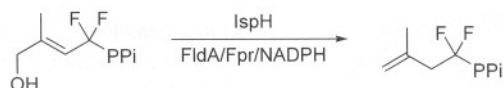
A. Jabri, C. B. Mason, Y. Sim,
S. Gambarotta,* T. J. Burchell,
R. Duchateau* — 9717–9721

Isolation of Single-Component
Trimerization and Polymerization
Chromium Catalysts: The Role of the
Metal Oxidation State



Enzyme Catalysis

Y. Xiao, P. Liu* 9722–9725

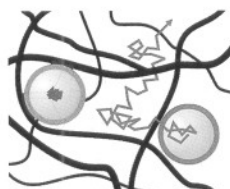


The last step of the deoxyxylulose phosphate pathway is catalyzed by IspH to synthesize two precursors for isoprenoid biosynthesis. The lack of a primary kinetic isotope effect at C₁ and enzymatic evaluation with a fluorinated analogue (see

scheme) suggest that the C₁-position is not involved in the IspH-catalyzed reaction. FldA = flavodoxin, Fpr = flavodoxin reductase, NADPH = nicotinamide adenine dinucleotide phosphate, PPi = P₂O₆³⁻.

Mucus-Penetrating Particles

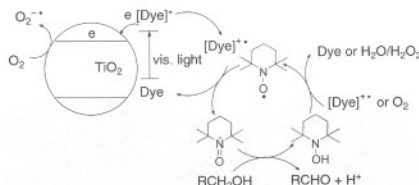
Y.-Y. Wang, S. K. Lai, J. S. Suk, A. Pace, R. Cone, J. Hanes* 9726–9729



Outsmarting the barrier: Conventional poly(ethylene glycol) (PEG) coated particles (green with light purple border) are immobilized in human mucus networks by adhesive interactions (red) with the mucus mesh (black lines). A dense, low molecular weight PEG coating (blue) uniquely endows nanoparticles with a mucoinert surface that enables their rapid mucus penetration (trajectory indicated by grey line).

Photocatalysis

M. Zhang, C. Chen, W. Ma,* J. Zhao* 9730–9733



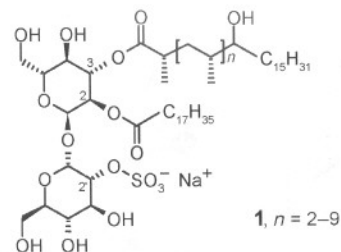
Like a differential gear: Upon irradiation with visible light, excited dye molecules inject electrons into TiO₂ and form dye radicals, which can oxidize TEMPO to TEMPO⁺, which in turn oxidizes alcohols in the presence of O₂ selectively to corresponding aldehydes. One reason for the selectivity is that the irradiation is downshifted to visible light.

Vaccines

J. Guiard, A. Collmann, M. Gilleron, L. Mori, G. De Libero, J. Prandi,* G. Puzo 9734–9738

Synthesis of Diacylated Trehalose Sulfates: Candidates for a Tuberculosis Vaccine

Able antigen analogues: Analogues of the mycobacterial sulfolipid antigen 1 isolated from *Mycobacterium tuberculosis* have been prepared by a short and general route. Some derivatives showed interesting immunogenic properties and activated cytotoxic T cells. Immunogenic analogues contained a chiral saturated or α,β -unsaturated polymethylated fatty acid with S configured stereogenic centers at the 3-position of the trehalose core.





A credit to donation: A diverse range of electrophilic addition reactions, conventionally carried out using Lewis acid catalysts, have been performed in electrophilic media without acidic reagents.

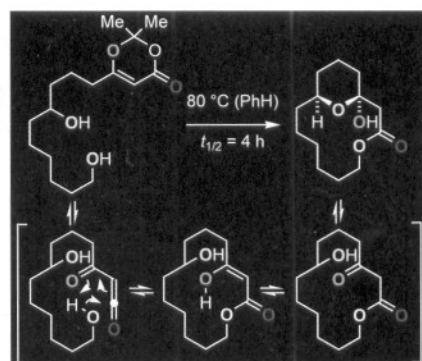
1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) acts as an efficient hydrogen-bond donor and highly polar solvent for a wide range of substrates in reactions with Si-capped π donors.

Electrophilic Reaction Media

M. O. Ratnikov, V. V. Tumanov,
W. A. Smit* 9739–9742

Lewis Acid Catalyst Free Electrophilic Alkylation of Silicon-Capped π Donors in 1,1,1,3,3,3-Hexafluoro-2-propanol

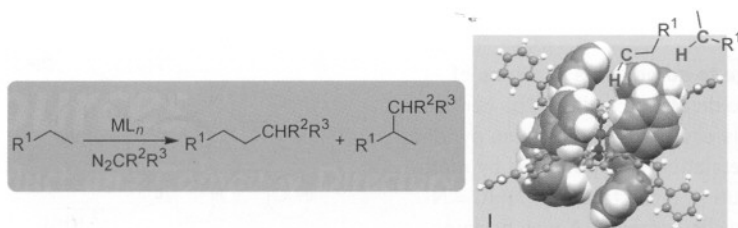
Two for one: Thermal generation of acylketenes in diol-containing substrates results in the title transformation. This transformation expands the scope of acylketene macrolactonizations and their application to the synthesis of complex macrolides. Triol and tetraol substrates have also been cyclized in highly regioselective fashion. Additionally, the challenging macrolactonization of a tertiary alcohol was achieved.



Synthetic Methods

T. R. Hoyer,* M. E. Danielson, A. E. May,
H. Zhao 9743–9746

Dual Macrolactonization/Pyran–Hemiketal Formation via Acylketenes: Applications to the Synthesis of (–)-Callipeltoside A and a Lyngbyaloside B Model System



Primary C–H bond activation! A Rh complex of bis-pocket porphyrin I catalyzes carbenoid insertion into the C–H bonds of *n*-alkanes with a primary/secondary selectivity (per C–H bond) of up to 11.4:1 (see picture). Enantioselective secondary

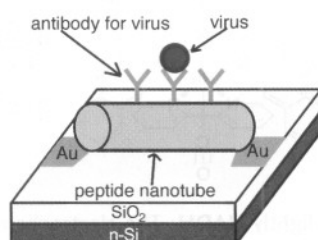
C–H bond functionalization catalyzed by a Rh complex of Halterman's chiral porphyrin features up to 93% *ee*. These reactions exhibit up to 6477 turnovers after the catalyst was recycled five times.

C–H Activation

H.-Y. Thu, G. S.-M. Tong, J.-S. Huang,
S. L.-F. Chan Q.-H. Deng,
C.-M. Che* 9747–9751

Highly Selective Metal Catalysts for Intermolecular Carbenoid Insertion into Primary C–H Bonds and Enantioselective C–C Bond Formation

A robust viral sensor was developed by bridging a pair of gold electrodes with antibody-coated peptide nanotubes. The nanotubes concentrated the target virus on their surface by molecular recognition between the antibody and the virus (see picture). The nanotubes fit perfectly within the electric field line distribution to enable the extremely sensitive impedimetric detection of viral particles.



Bionanotechnology

R. de la Rica,* E. Mendoza,
L. M. Lechuga, H. Matsui* 9752–9755

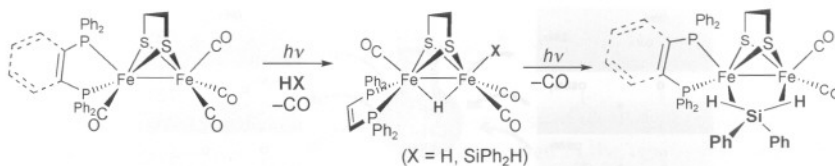
Label-Free Pathogen Detection with Sensor Chips Assembled from Peptide Nanotubes

Hydrogenase Models

Z. M. Heiden, G. Zampella, L. De Gioia,*
T. B. Rauchfuss* — 9756–9759



[FeFe]-Hydrogenase Models and
Hydrogen: Oxidative Addition of
Dihydrogen and Silanes



Super model: Diiron dithiolates exist in nature in [FeFe]-hydrogenase, for the purpose of making or oxidizing molecular hydrogen. Evidence for how H₂ interacts with diiron complexes has been realized

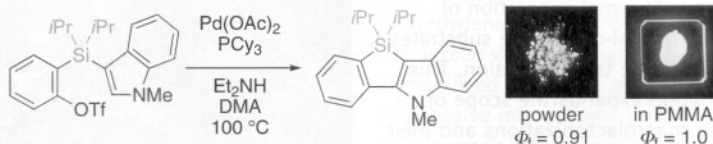
using model diiron dithiolato carbonyl complexes. The pathway for this interaction has been elucidated computationally as well as synthetically, by using silanes in place of H₂.

Synthetic Methods

M. Shimizu,* K. Mochida,
T. Hiyama — 9760–9764



Modular Approach to Silicon-Bridged
Biaryls: Palladium-Catalyzed
Intramolecular Coupling of
2-(Arylsilyl)aryl Triflates



Bridge of Si: Intramolecular direct arylation of 2-(arylsilyl)aryl triflates is catalyzed smoothly by Pd(OAc)₂/PCy₃ in the presence of Et₃NH in dimethylacetamide (DMA), giving rise to the corresponding silicon-bridged biaryls in good to excellent

yields. The new approach has led to the synthesis of a silicon-bridged 2-phenylindole (see scheme) that exhibits blue photoluminescence in the solid state with extremely high quantum yields.

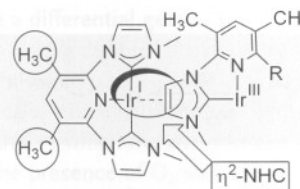
Carbene Complexes

A. A. Danopoulos,* D. Pugh,
J. A. Wright — 9765–9767



“Pincer” Pyridine–Dicarbene–Iridium
Complexes: Facile C–H Activation and
Unexpected η²-Imidazol-2-ylidene
Coordination

A bridge to somewhere: A series of pyridine dicarbene iridium “pincer” complexes is easily accessible when pyridine ring metalation is suppressed by methyl substitution (see structure; NHC = N-heterocyclic carbene). A new bridging binding mode of the imidazol-2-ylidene heterocycle, involving η²-alkene-like coordination, has been observed crystallographically.

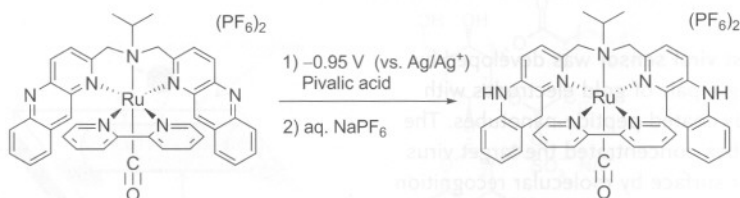


Electrochemical Reduction

M. Kimura, K. Tanaka* — 9768–9771

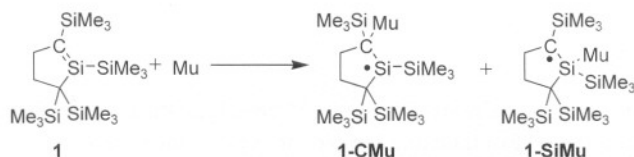


Synthesis and Electrochemical Reduction
of a Ruthenium Complex Bearing an
N,N-Bis[(benzo[g][1,5]naphthyridin-2-yl)-
methyl]propane-2-amine Ligand as an
NAD⁺/NADH-Type Redox Site



Going slightly NADH: The electrochemical reduction of [Ru(bbnma)(bpy)(CO)](PF₆)₂ (bbnma = N,N-bis[(benzo[g][1,5]naphthyridin-2-yl)methyl]propane-2-

amine, bpy = 2,2'-bipyridine) in the presence of pivalic acid gave [Ru(bbnmaH₄)(bpy)(CO)](PF₆)₂, the NADH-type product of a four-electron reduction.



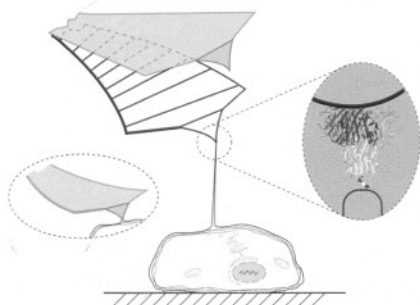
Taking the silenic route: Addition of a hydrogen atom analogue, muonium (Mu), to stable silene **1** gives rise to two distinct radical species, **1-CMu** and **1-SiMu**, allowing the relative reactivity of silenic carbon and silicon atoms to be

probed. The former is the first reported example of a muoniated silyl radical. The radical species are detected by muon spin rotation and resonance spectroscopy (μSR).

Relative Reactivity

B. M. McCollum, T. Abe, J.-C. Brodovitch, J. A. C. Clyburne, T. Iwamoto, M. Kira, P. W. Percival,* R. West — **9772–9774**

Probing the Reactivity of a Stable Silene Using Muonium



The name's Bond: Separated cells form membranous nanotubes whose tips are tethered by adhesive bonds (see picture). The lifetime of receptor–ligand interactions can be measured by using membrane nanotubes of living cells as constant force actuators. Because the nanotubes are extruded from living cells at conditions approaching the physiological, cellular processes can be both studied and utilized.

Cellular Adhesion

M. Krieg, J. Helenius, C.-P. Heisenberg, D. J. Müller* — **9775–9777**

A Bond for a Lifetime: Employing Membrane Nanotubes from Living Cells to Determine Receptor–Ligand Kinetics



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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