Service

Author Profile

„I like refereeing because it allows me to deploy my fault-finding talent.
The biggest problem that scientists face is being misjudged geniuses. …“
This and more about Martin Jansen can be found on page 8420.

News

D. K. Smith

L. Cronin

P. L. Arnold

P. R. Unwin

J. R. Durrant

H. L. Anderson

T. M. Swager

A. K. Cheetham

Books

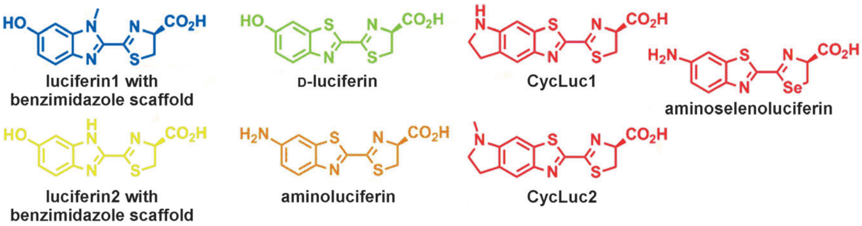
© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Highlights

Bioluminescence

Y.-Q. Sun, J. Liu, P. Wang, J. Zhang, W. Guo* ________ **8428 – 8430**

D-Luciferin Analogues: a Multicolor Toolbox for Bioluminescence Imaging



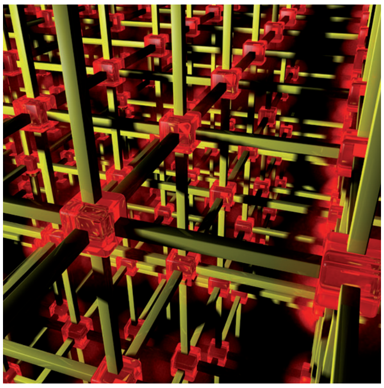
Colorful mixture: Three types of luciferin analogues, that is, alkylaminoluciferins, aminoselenoluciferin, and luciferins with a benzimidazole scaffold, have been reported (see scheme). These analogues show excellent bioluminescent properties and great potential in bioluminescence imaging.

Metal–Organic Frameworks

P. Falcaro, S. Furukawa* ____ **8431 – 8433**

Doping Light Emitters into Metal–Organic Frameworks

Space division with red cubes: Doping metal–organic frameworks with another metal component gives a further opportunity to tune their properties. Recent work successfully introduced europium into the inorganic nodes of frameworks. Although the doping element does not affect the framework topology, highly improved emissive performance was measured thanks to the intrinsic red emission of europium.

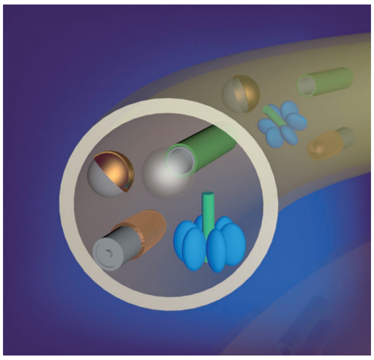


Minireviews

Intelligent Nanorobots

S. Sengupta, M. E. Ibele, A. Sen* ________ **8434 – 8445**

Fantastic Voyage: Designing Self-Powered Nanorobots

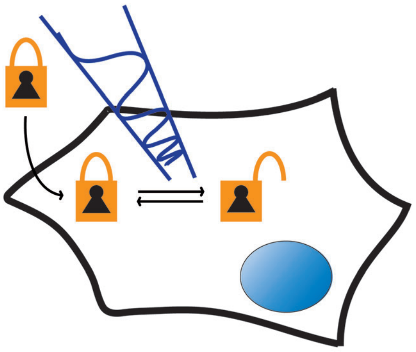


Vision of the future? Nanorobots are artificial nanostructures that can use chemical fuels to move autonomously over long distances and simultaneously perform complex tasks in cooperation. These motors can be directed by chemical and light gradients, pick up and deliver cargo, and exhibit emergent collective behavior. Potential applications range from the real-time reconfiguration of material assemblies to the targeted modular repair of cellular components.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 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*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (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.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Reviews



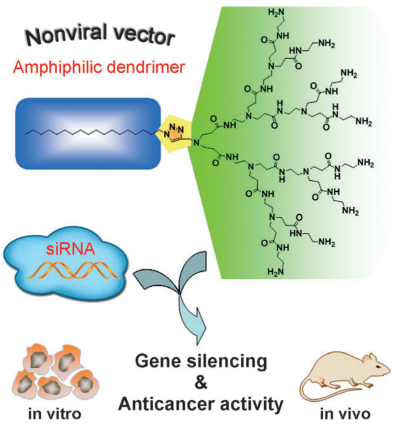
Spot on! Systems which can be regulated by using light as a trigger can be used for very sophisticated experiments in which aspects of space, time, or extent of activation are to be studied. Irreversible photocleavage, reversible photoswitching, and genetically expressible systems are the three possibilities for coupling the trigger to an effect.

Biochemical Photoswitches

C. Brieke, F. Rohrbach, A. Gottschalk,*
G. Mayer,* A. Heckel* ______ **8446 – 8476**

Light-Controlled Tools

Communications



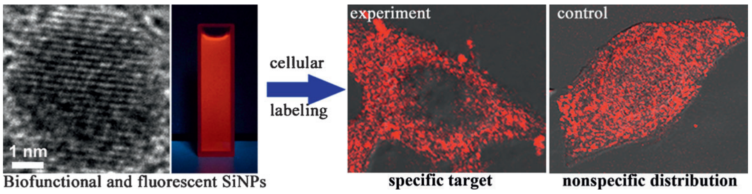
An amphiphilic dendrimer bearing a hydrophobic alkyl chain and hydrophilic poly(amidoamine) dendrons is able to combine the advantageous features of lipid and dendrimer vectors to deliver a heat shock protein 27 siRNA and produce potent gene silencing and anticancer activity in vitro and in vivo in a prostate cancer model (see picture). This dendrimer can be used alternatively for treating various diseases.

Drug Design

T. Yu, X. Liu, A.-L. Bolcato-Bellemin,
Y. Wang, C. Liu, P. Erbacher, F. Qu,
P. Rocchi, J.-P. Behr,
L. Peng* ______ **8478 – 8484**

An Amphiphilic Dendrimer for Effective Delivery of Small Interfering RNA and Gene Silencing In Vitro and In Vivo

Frontispiece



Protective shell: A microwave-assisted method allows rapid production of biofunctional and fluorescent silicon nanoparticles (SiNPs), which can be used for cell labeling (see picture). Such SiNPs feature excellent aqueous dispersibility, are strongly fluorescent, storable, photostable, stable at different pH values, and biocompatible. The method opens new avenues for designing multifunctional SiNPs and related silicon nanostructures.

Nanoparticles

Y. L. Zhong, F. Peng, X. P. Wei, Y. F. Zhou,
J. Wang, X. X. Jiang, Y. Y. Su, S. Su,
S. T. Lee,* Y. He* ______ **8485 – 8489**

Microwave-Assisted Synthesis of Biofunctional and Fluorescent Silicon Nanoparticles Using Proteins as Hydrophilic Ligands

Inside Cover

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

The German Chemical Society (GDCh) invites you to:

Angewandte 125 Jahre Anniversary Symposium

GDCh

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

Speakers


Carolyn R. Bertozzi


François Diederich


Alois Fürstner


Roald Hoffmann
(Nobel Prize 1981)


Susumu Kitagawa


Jean-Marie Lehn
(Nobel Prize 1987)


E.W. “Bert” Meijer


Frank Schirrmacher
(Publisher, *FAZ*)


Robert Schlögl


George M. Whitesides


Ahmed Zewail
(Nobel Prize 1999)

More information:

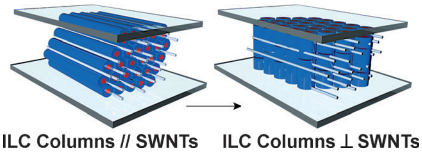
angewandte.org/symposium

Freie Universität Berlin

WILEY-VCH

GDCh
Gesellschaft
Deutscher Chemiker

PSJ_12_42497_5_gu



Orient and conduct: Triphenylene-based discotic ionic liquid crystals (ILCs) with six imidazolium ion pendants can disperse pristine single-walled carbon nanotubes (SWNTs). When the ILC is columnarly assembled, doping with SWNTs results in macroscopic homeotropic columnar orientation. Combination of shear and annealing treatments gives rise to three different orientation states, which determine the anisotropy of electrical conduction.

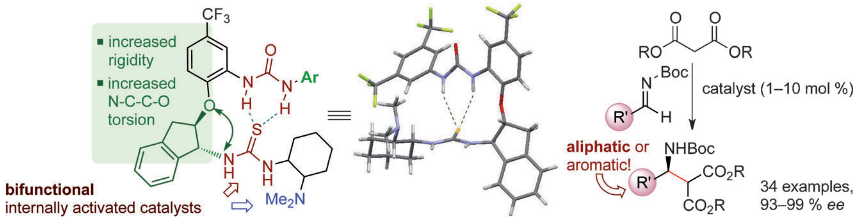
Hybrid Nanomaterials

VIP

J. J. Lee, A. Yamaguchi, M. A. Alam, Y. Yamamoto,* T. Fukushima, K. Kato, M. Takata, N. Fujita, T. Aida* **8490 – 8494**

Discotic Ionic Liquid Crystals of Triphenylene as Dispersants for Orienting Single-Walled Carbon Nanotubes

Back Cover



Hold them tight: Guided by X-ray structures, bifunctional thiourea catalysts containing an activating intramolecular hydrogen bond were redesigned. The new catalysts were used to effect a highly enantioselective Mannich reaction between malonates and both aliphatic and aromatic imines (see scheme; Boc = *tert*-butoxycarbonyl).

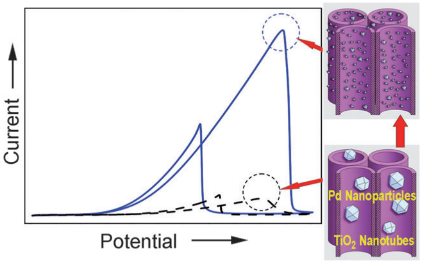
Organocatalysis

N. Probst, Á. Madarász, A. Valkonen, I. Pápai, K. Rissanen, A. Neuvonen, P. M. Pihko* **8495 – 8499**

Cooperative Assistance in Bifunctional Organocatalysis: Enantioselective Mannich Reactions with Aliphatic and Aromatic Imines

---

Improved performance through milling: A method for enhancing the catalytic activity of supported metal nanoparticles is reported. This method enhances the activity for the ethanol electro-oxidation of a supported palladium catalyst (see picture). The much higher catalytic performance is ascribed to the increased electrochemically active surface area as well as the generation of high-index facets at the milled nanoparticle surface.



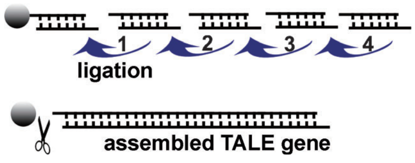
Electrocatalysis

Y. X. Chen, A. Lavacchi,* S. P. Chen, F. di Benedetto, M. Bevilacqua, C. Bianchini, P. Fornasiero, M. Innocenti, M. Marelli, W. Oberhauser, S. G. Sun,* F. Vizza* **8500 – 8504**

Electrochemical Milling and Faceting: Size Reduction and Catalytic Activation of Palladium Nanoparticles

---

A TALE of two assays: Transcription activator-like effectors (TALEs) are programmable proteins that can specifically recognize a DNA sequence. Previous strategies for the synthesis of TALEs were complicated and time-consuming. The solid-phase synthesis strategy demonstrated here (see scheme) allows quick and simple purification of the ligation product.



Solid-Phase Synthesis

Z. Wang, J. Li, H. Huang, G. Wang, M. Jiang, S. Yin, C. Sun, H. Zhang, F. Zhuang,* J. Xi* **8505 – 8508**

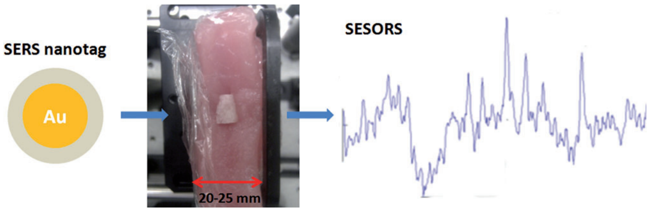
An Integrated Chip for the High-Throughput Synthesis of Transcription Activator-like Effectors

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Nano-Bio-Imaging

H. Xie, R. Stevenson, N. Stone, A. Hernandez-Santana, K. Faulds, D. Graham* ——— **8509 – 8511**

Tracking Bisphosphonates through a 20 mm Thick Porcine Tissue by Using Surface-Enhanced Spatially Offset Raman Spectroscopy

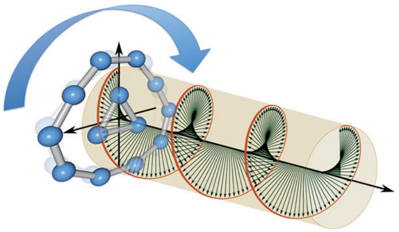


Track it down: A recognized surface-enhanced Raman scattering (SERS) nanotag signal was monitored from a thin, dispersed layer of bisphosphonate-functionalized nanotags on a bone sample, through a 20 mm thick specimen of porcine muscle tissue by surface-enhanced spatial offset Raman spectroscopy (SESORS; see picture). The result demonstrates the great potential for non-invasive in vivo bisphosphonate drug tracking.

Molecular Motors

J. Zhang,* A. P. Sergeeva, M. Sparta, A. N. Alexandrova* ——— **8512 – 8515**

B_{13}^+: A Photodriven Molecular Wankel Engine

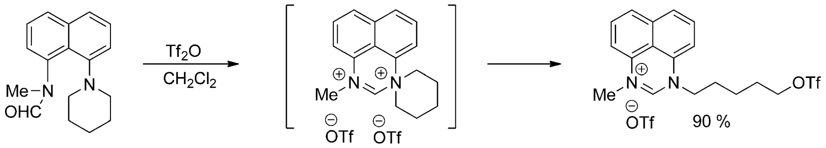


Revved-up rotary: A molecular Wankel motor, the dual-ring structure B_{13}^+, is driven by circularly-polarized infrared electromagnetic radiation. Calculations show that this illumination leads to a guided unidirectional rotation of the outer ring, which is achieved with rotational frequency of the order of 300 GHz.

Superelectrophiles

L. S. Kovacevic, C. Idziak, A. Markevicius, C. Scullion, M. J. Corr, A. R. Kennedy, T. Tuttle,* J. A. Murphy* ——— **8516 – 8519**

Superelectrophilic Amidine Dications: Dealkylation by Triflate Anion



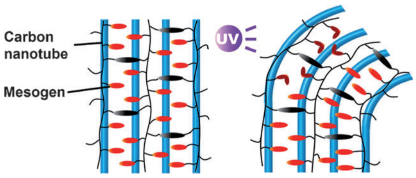
Superelectrophiles: Formamides were designed that when treated with triflic anhydride would be transformed into superelectrophilic amidine dications. These dications were so electrophilic that they underwent in situ dealkylation by the triflate anion (see scheme; Tf = trifluoromethanesulfonyl). DFT calculations were used to determine the mechanistic details of the dealkylation reaction.

Photomechanical Actuation

X. Sun, W. Wang, L. Qiu, W. Guo, Y. Yu, H. Peng* ——— **8520 – 8524**

Unusual Reversible Photomechanical Actuation in Polymer/Nanotube Composites

An azobenzene-containing liquid crystalline polymer/carbon nanotube composite strip was synthesized that shows rapid and reversible deformation under UV irradiation. The aligned nanotubes also provide the composite with much higher mechanical strength than pure liquid crystalline polymers and a very high electrical conductivity.

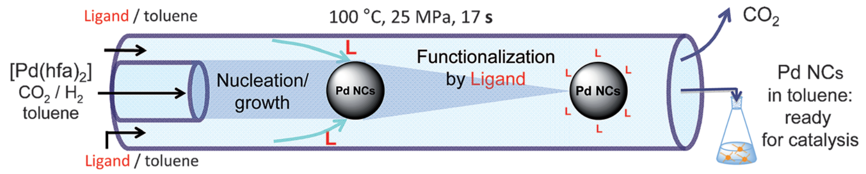


© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Nanostructures

T. Gendrineau, S. Marre, M. Vaultier,
M. Pucheault,*
C. Aymonier* ———— **8525 – 8528**

Microfluidic Synthesis of Palladium Nanocrystals Assisted by Supercritical CO_2: Tailored Surface Properties for Applications in Boron Chemistry



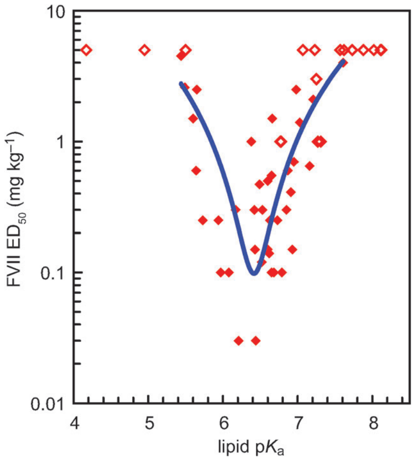
On the surface: A library of organic–inorganic hybrid palladium nanocrystals was synthesized using continuous supercritical microfluidic technology. The nanocatalysts show moderate to excellent activities towards C_{Ar}–B and C_{Ar}–C_{Ar} bond-forming reactions, thus illustrating the relationship between surface properties and modulated catalytic activity.

siRNA Delivery

M. Jayaraman,* S. M. Ansell, B. L. Mui,
Y. K. Tam, J. Chen, X. Du, D. Butler,
L. Eltepu, S. Matsuda, J. K. Narayanannair,
K. G. Rajeev, I. M. Hafez, A. Akinc,
M. A. Maier, M. A. Tracy, P. R. Cullis,
T. D. Madden, M. Manoharan,
M. J. Hope* ———— **8529 – 8533**

Maximizing the Potency of siRNA Lipid Nanoparticles for Hepatic Gene Silencing In Vivo

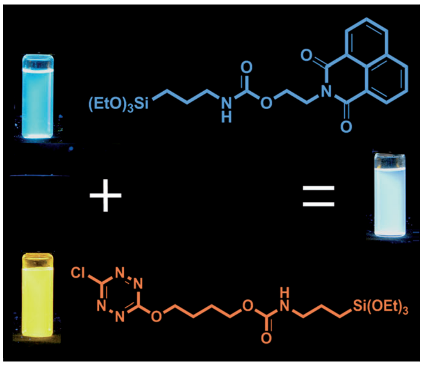
Special (lipid) delivery: The role of the ionizable lipid pK_a in the in vivo delivery of siRNA by lipid nanoparticles has been studied with a large number of head group modifications to the lipids. A tight correlation between the lipid pK_a value and silencing of the mouse FVII gene (FVII ED_{50}) was found, with an optimal pK_a range of 6.2–6.5 (see graph). The most potent cationic lipid from this study has ED_{50} levels around 0.005 mg kg^{-1} in mice and less than 0.03 mg kg^{-1} in non-human primates.



Fluorescent Nanoparticles

J. Malinge, C. Allain,* A. Brosseau,
P. Audebert* ———— **8534 – 8537**

White Fluorescence from Core–Shell Silica Nanoparticles



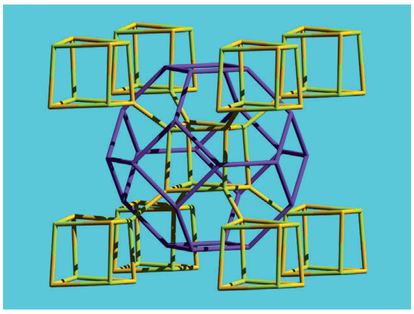
Into the white: Encapsulation of a naphthalimide moiety in the core of silica nanoparticles afforded nanospheres with a strong green excimeric emission. Together with the blue emission of the monomeric naphthalimide and the yellow fluorescence of the tetrazine acceptor on the outer shell, the added contributions provide intense white fluorescence upon 330 nm UV excitation.

Metal–Organic Frameworks

F. Bu, Q.-P. Lin, Q.-G. Zhai, L. Wang,
T. Wu, S.-T. Zheng, X. Bu,*
P. Feng* ———— **8538 – 8541**

Two Zeolite-Type Frameworks in One Metal–Organic Framework with $Zn_{24}@Zn_{104}$ Cube-in-Sodalite Architecture

Two in one: A metal–organic framework obtained from three different inorganic building blocks (tetrameric Zn_4O, trimeric Zn_3OH, and monomeric Zn) posseses a nested cage-in-cage and framework-in-framework architecture (see picture). 24 Zn_4O tetramers and eight Zn monomers form a sodalite cage into which a cubic cage made from eight $Zn_3(OH)$ trimers is nestled. Eight monomeric Zn^{2+} centers interconnect these two cages.

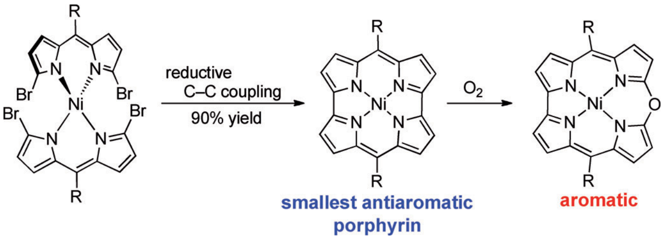


© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Antiaromatic Porphyrins

T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi,* H. Shinokubo* ———— **8542–8545**

Gram-Scale Synthesis of Nickel(II) Norcorrole: The Smallest Antiaromatic Porphyrinoid



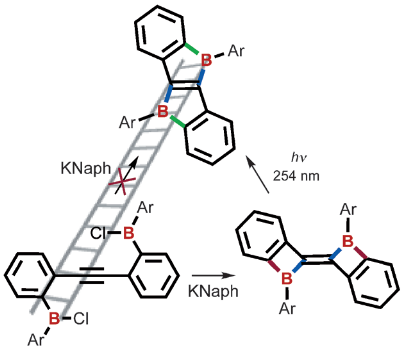
Small is beautiful: A ring-contracted sister of porphyrin, norcorrole, has been synthesized efficiently as a stable molecule by a nickel-templated strategy. The norcorrole complex is stable but exhibits a distinct antiaromatic character according to the Hückel rule. Oxidation of the norcorrole complex provides an aromatic oxacorrole complex.

Boron Heterocycles

J. F. Araneda, B. Neue, W. E. Piers,* M. Parvez ———— **8546–8550**

Photochemical Synthesis of a Ladder Diborole: A New Boron-Containing Conjugate Material

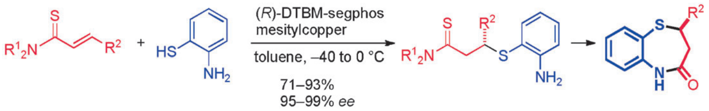
Climbing the ladder: Reductive cyclization of alkynyl haloboranes lead to the bis-benzocycloborabutylidene rather than the expected ladder diborole, despite the former being much less thermodynamically favored. Photochemical conversion to the ladder diborole was, however, quite facile upon irradiation at 254 nm.



Synthetic Methods

T. Ogawa, N. Kumagai,* M. Shibasaki* ———— **8551–8554**

Catalytic Asymmetric Conjugate Addition of Thiols to α,β-Unsaturated Thioamides: Expeditious Access to Enantioenriched 1,5-Benzothiazepines

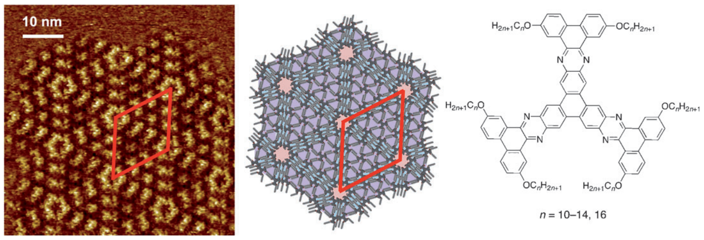


Softly does it: The title reaction proceeded under proton transfer conditions with a catalyst prepared from commercially available reagents to afford the desired product in high enantioselectivity. The reaction was compatible with a free amino group, thus allowing for expeditious access to enantiomerically enriched 1,5-benzothiazepines, which are important chemical entities in medicinal chemistry.

Supramolecular Networks

S.-S. Jester,* E. Sigmund, L. M. Röck, S. Höger* ———— **8555–8559**

Hierarchical Self-Assembly of Polycyclic Heteroaromatic Stars into Snowflake Patterns



Seeing stars: The two-dimensional patterns of the polycyclic heteroaromatic star molecules **1** on graphite vary with the side chain length. For $n=12$, frustrated self-assembly leads to hierarchically organized superstructures: up to 10 molecules form triangular aggregates which pack densely into hexagonal patterns with very large (15.5 nm) lattice constants.

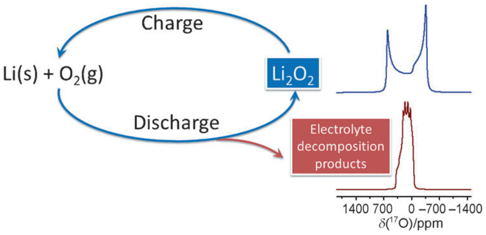
© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Lithium–Oxygen Batteries

M. Leskes, N. E. Drewett, L. J. Hardwick,
P. G. Bruce, G. R. Goward,
C. P. Grey* ______ 8560 – 8563

Direct Detection of Discharge Products in Lithium–Oxygen Batteries by Solid-State NMR Spectroscopy

Inside Back Cover

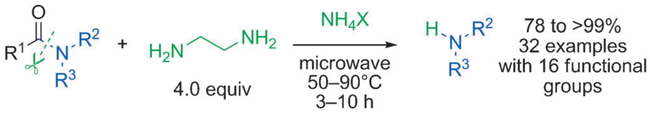


A closer look: Solid-state ^{7}Li and ^{17}O NMR spectroscopy is a valuable tool in the characterization of products formed in the lithium–oxygen battery, a necessary step in the development of a viable cell. Since lithium peroxide, the desired discharge product, has a unique ^{17}O NMR signature, it can be clearly identified.

Protecting Groups

Y. Shimizu, H. Morimoto, M. Zhang,
T. Ohshima* ______ 8564 – 8567

Microwave-Assisted Deacylation of Unactivated Amides Using Ammonium-Salt-Accelerated Transamidation

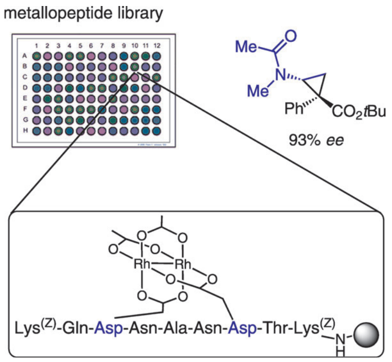


The combination of an ammonium salt and ethylenediamine promotes deacylation of a variety of unactivated amides to give the corresponding amines in high yields without the use of strong acids or bases. The reactions proceed without special care regarding air and moisture, and tolerate a wide range of functional groups.

Catalyst Screening

R. Sambasivan, Z. T. Ball* __ 8568 – 8572

Screening Rhodium Metallopeptide Libraries "On Bead": Asymmetric Cyclopropanation and a Solution to the Enantiomer Problem

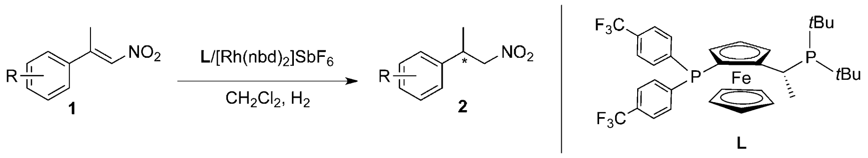


Searching with a beady eye: A high-throughput, on-bead screen of rhodium metallopeptide catalysts was developed in a 96-well format for asymmetric cyclopropanation. Different sequences of natural L-amino acids have been identified that produce opposite product enantiomers (see picture). In addition to styrene derivatives, high enantioselectivity is observed for vinyl ether and vinyl amine derivatives.

Asymmetric Hydrogenation

S. Li, K. Huang, B. Cao, J. Zhang, W. Wu,*
X. Zhang* ______ 8573 – 8576

Highly Enantioselective Hydrogenation of β,β-Disubstituted Nitroalkenes



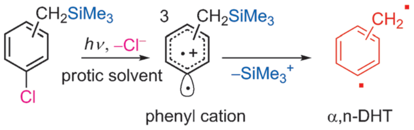
Building the building blocks: A highly enantioselective hydrogenation of β-aryl-β-alkyl disubstituted nitroalkenes **1** has been developed. This method results in enantiomerically pure nitroalkanes **2**, which are versatile precursors for chemical synthesis.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Radicals

S. Protti, D. Ravelli, B. Mannucci,
A. Albini, M. Fagnoni* ____ **8577 – 8580**

α,*n*-Didehydrotoluenes by Photoactivation of (Chlorobenzyl)-trimethylsilanes: An Alternative to Enyne–Allenes Cyclization

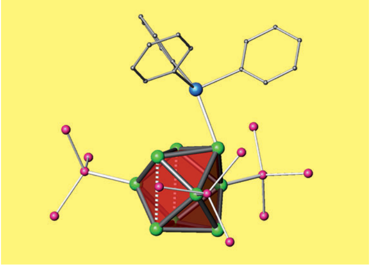


Doubly radical: A novel entry to α,*n*-didehydrotoluene (DHT) diradicals is disclosed and proceeds through the photochemical activation of (chlorobenzyl)-trimethylsilanes with chloride loss and elimination of the $SiMe_3^+$ group (see scheme). The products formed in solution are indicative of the intermediacy of the three isomers of the α,*n*-DHT.

Zintl Clusters

F. Li, A. Muñoz-Castro,
S. C. Sevov* ____________ **8581 – 8584**

$[Ge_9\{Si(SiMe_3)_3\}_3\{SnPh_3\}]$:
A Tetrasubstituted and Neutral Deltahedral Nine-Atom Cluster



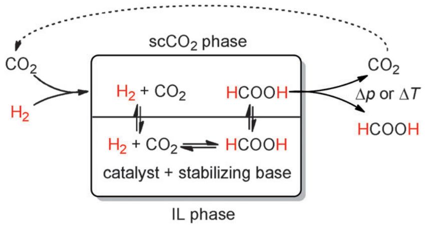
Reaching neutral territory: The title compound, the first tetrasubstituted deltahedral Zintl cluster, is no longer an ion (see picture; Ge green, Si purple, Sn blue). It is a neutral molecule formed by a reaction of the trisilylated anion with Ph_3SnCl.

CO_2 Hydrogenation

S. Wesselbaum, U. Hintermair,
W. Leitner* ____________ **8585 – 8588**

Continuous-Flow Hydrogenation of Carbon Dioxide to Pure Formic Acid using an Integrated $scCO_2$ Process with Immobilized Catalyst and Base

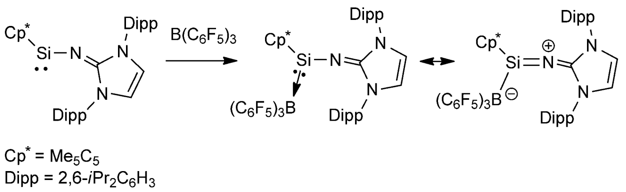
Dual role for CO_2: Pure formic acid can be obtained continuously by hydrogenation of CO_2 in a single processing unit (see scheme). An immobilized ruthenium organometallic catalyst and a nonvolatile base in an ionic liquid (IL) are combined with supercritical CO_2 as both reactant and extractive phase.



Silylene Compounds

S. Inoue,* K. Leszczyńska __ **8589 – 8593**

An Acyclic Imino-Substituted Silylene: Synthesis, Isolation, and its Facile Conversion into a Zwitterionic Silaimine

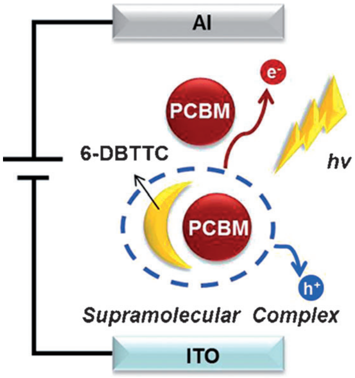


A new type of Si(II): A novel silylene stabilized by a Cp* and an imidazolin-2-iminato ligand has been prepared using two different methods (see scheme). The X-ray crystallographic structure shows that the silicon(II) center is coordinated to an η^2-Cp* ligand and the nitrogen atom of an imidazolin-2-iminato ligand. This silylene easily reacts with $B(C_6F_5)_3$ to give a stable borane adduct having a zwitterionic resonance structure.

Solar Cells

S. J. Kang, J. B. Kim, C.-Y. Chiu, S. Ahn, T. Schiros, S. S. Lee, K. G. Yager, M. F. Toney, Y.-L. Loo, C. Nuckolls* ________ **8594 – 8597**

A Supramolecular Complex in Small-Molecule Solar Cells based on Contorted Aromatic Molecules

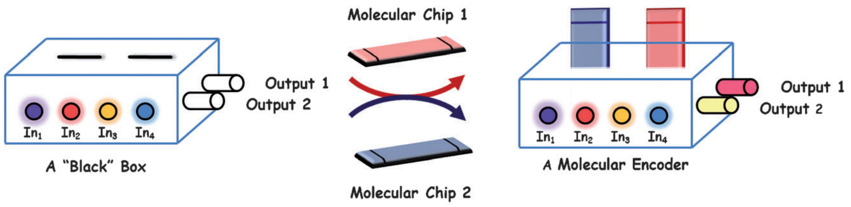


“Ball and socket” motif: The contorted dibenzotetrathienocoronene (6-DBTTC) forms a complex with the C_{70} fullerene $PC_{70}BM$ embedded in an amorphous phase of $PC_{70}BM$. The materials are processable into organic solar cells in solution. The power conversion efficiency is maximal when there is a 1:2 molar ratio of 6-DBTTC to $PC_{70}BM$. Formation of the supramolecular complex directly affects charge separation in the active layer.

Molecular Encoder

G. de Ruiter, M. E. van der Boom* ________ **8598 – 8601**

Orthogonal Addressable Monolayers for Integrating Molecular Logic



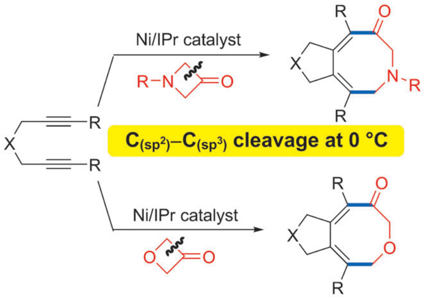
Plug and play: The mimicking of integrated circuits by using two individual monolayers (molecular chips) is shown. These monolayers can be individually addressed using identical inputs. Upon combination of their optical outputs, the input/output characteristics of a molecular encoder is obtained. Since the encoder functionality is only displayed when both chips are active, the device behaves according to a plug-and-play principle (In = input; see picture).

Cycloaddition Reactions

P. Kumar, K. Zhang, J. Louie* ________ **8602 – 8606**

An Expeditious Route to Eight-Membered Heterocycles By Nickel-Catalyzed Cycloaddition: Low-Temperature C_{sp^2}–C_{sp^3} Bond Cleavage

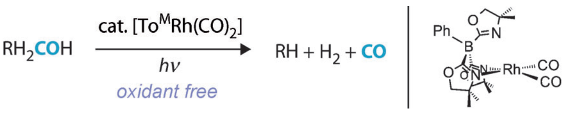
A cool break: 3-Azetidinone and a variety of diynes undergo a cycloaddition reaction catalyzed by Ni/IPr to give dihydroazocine compounds (see scheme; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidene). The reaction involves a challenging C_{sp^2}–C_{sp^3} bond cleavage step, yet, surprisingly, proceeds at low temperature.



Photocatalysis

H.-A. Ho, K. Manna, A. D. Sadow* ________ **8607 – 8610**

Acceptorless Photocatalytic Dehydrogenation for Alcohol Decarbonylation and Imine Synthesis



It has come to light: Renewed interest in conversions of highly oxygenated materials has motivated studies of the organometallic-catalyzed photocatalytic dehydrogenative decarbonylation of primary alcohols into alkanes, CO, and H_2 (see scheme). Methanol, ethanol, benzyl alcohol, and cyclohexanemethanol are readily decarbonylated. The photocatalysts are also active for amine dehydrogenation to give *N*-alkyl aldimines and H_2.

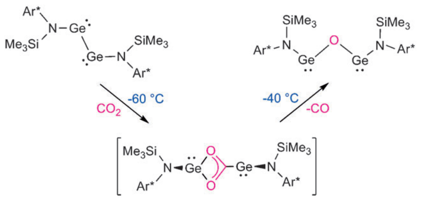
© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Green Chemistry

J. Li, M. Hermann, G. Frenking,* C. Jones* ________ **8611 – 8614**

The Facile Reduction of Carbon Dioxide to Carbon Monoxide with an Amido-Digermyne

Taking the fizz out: A digermyne compound with a Ge–Ge single bond has been shown to quantitatively reduce CO_2 to CO at temperatures as low as −40 °C. The mechanism of this unprecedented reaction has been probed by spectroscopic and computational techniques and involves a metastable intermediate (see picture; $Ar^* = C_6H_2\{C(H)Ph_2\}_2Me\text{-}2,6,4$).

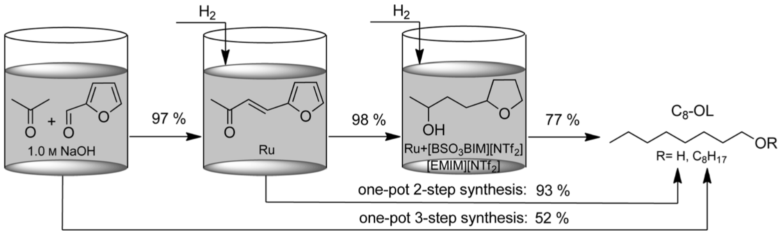


Biogenic Alcohols

J. Julis, W. Leitner* ________ **8615 – 8619**

Synthesis of 1-Octanol and 1,1-Dioctyl Ether from Biomass-Derived Platform Chemicals

Front Cover



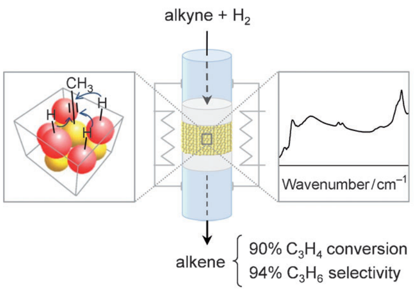
The happy medium: A new catalytic pathway for the synthesis of the linear primary C_8 alcohol products 1-octanol and dioctyl ether from furfural and acetone has been developed using retrosynthetic analysis. This opens a general strategy for the synthesis of medium-chain-length alcohols from carbohydrate feedstock.

Heterogeneous Catalysis

G. Vilé, B. Bridier, J. Wichert, J. Pérez-Ramírez* ________ **8620 – 8623**

Ceria in Hydrogenation Catalysis: High Selectivity in the Conversion of Alkynes to Olefins

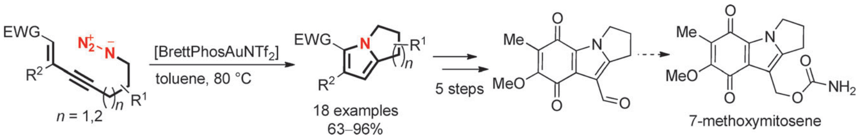
Active and selective: Ceria shows a high activity and selectivity in the gas-phase hydrogenation of alkynes to olefins (see picture). This unprecedented behavior has direct impact on the purification of olefin streams and, more importantly, it opens new perspectives for exploring this fascinating oxide as a catalyst for the selective hydrogenation of other functional groups.



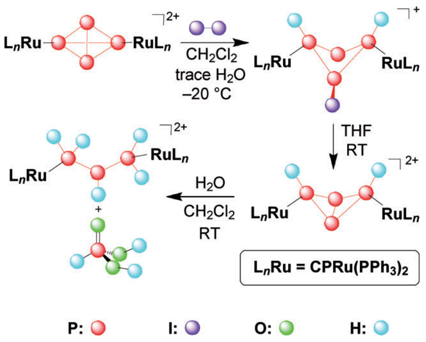
Gold Catalysis

Z.-Y. Yan, Y. Xiao, L. Zhang* **8624 – 8627**

Gold-Catalyzed One-Step Construction of 2,3-Dihydro-1*H*-Pyrrolizines with an Electron-Withdrawing group in the 5-position: A Formal Synthesis of 7-Methoxymitosene



What a ring formation! Bicyclic dihydropyrrolizines with an electron-withdrawing group (EWG) at the 5-position are formed in one step from linear azidoenynes under gold catalysis. This novel route involves the use of azide as a nitrene precursor, electronically-controlled regioselectivity, and the generation of destabilized 1-azapentadienium ions and their pericyclic reactions. This method was used for a formal synthesis of 7-methoxymitosene (see scheme).



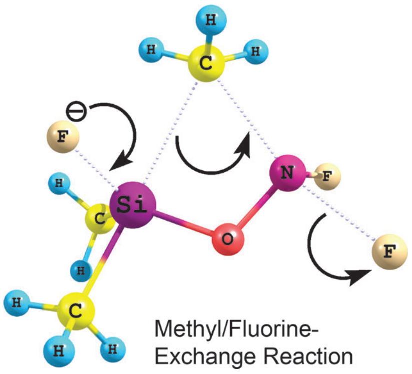
Double stabilization: Previously unknown polyphosphorus compounds are obtained by activation of white phosphorus (P_4) coordinated between two CpRu(PPh_3)$_2$ moieties with iodine, and subsequent hydrolysis. The polyphosphorus compounds (P_4H_2I, P_4H_2, P_3H_5; see scheme, Cp = cyclopentadienyl) are all stabilized by coordination to two ruthenium centers.

Polyphosphorus Compounds

P. Barbaro, C. Bazzicalupi, M. Peruzzini, S. Seniori Costantini, P. Stoppioni* ______ **8628 – 8631**

Iodine Activation of Coordinated White Phosphorus: Formation and Transformation of 1,3-Dihydride-2-iodidecyclotetraphosphane

---



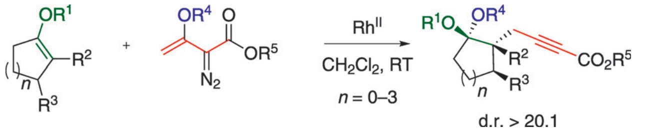
Exchange Me for a fluorine: Trimethylsiloxide ions in the presence of NF_3 in the gas phase undergo an unusual and sequential metathesis-type reaction wherein methyl groups are exchanged for fluorine. Theoretical calculations suggest that the reaction proceeds by a three-step internal-nucleophilic-displacement mechanism which features a pentacoordinated siliconate species (see picture) as a transition state rather than as an intermediate.

Gas-Phase Reactions

T. C. Correra, J. M. Riveros* . **8632 – 8635**

Sequential Methyl–Fluorine Exchange Reactions of Siloxide Ions in the Gas Phase

---



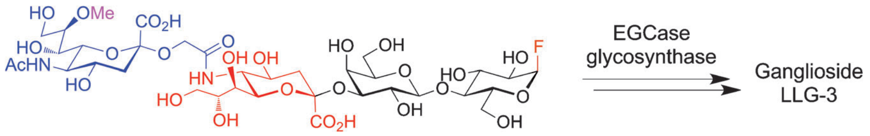
Siloxy group migration: A rhodium(II) carbenoid approach has been developed for the synthesis of alkynoates (see scheme). This transformation combines the addition of enol ethers at the vinylogous position of β-siloxy-substituted vinyldiazo derivatives with a siloxy group migration to give the products as single diastereomers.

Rhodium Catalysis

D. Valette, Y. Lian, J. P. Haydek, K. I. Hardcastle, H. M. L. Davies* ______ **8636 – 8639**

Alkynoate Synthesis through the Vinylogous Reactivity of Rhodium(II) Carbenoids

---



An LLG-3 oligosaccharide–fluoride (see scheme) can be assembled chemoenzymatically and readily coupled with various sphingosines by an engineered endoglycoceramidase glycosynthase. The *lyso* ganglioside products are acylated to generate the individual isomers identified in the heterogeneous natural isolates, as well as modified glycosphingolipids.

Carbohydrates

J. R. Rich,* S. G. Withers ___ **8640 – 8643**

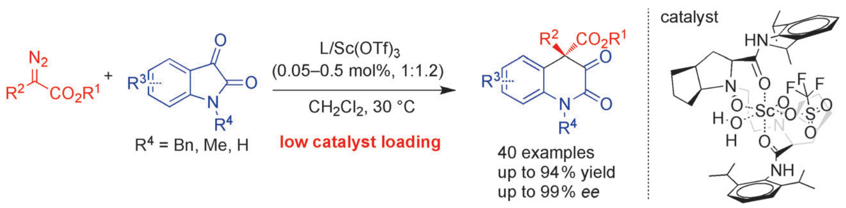
A Chemoenzymatic Total Synthesis of the Neurogenic Starfish Ganglioside LLG-3 Using an Engineered and Evolved Synthase

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Asymmetric Catalysis

W. Li, X. H. Liu, X. Y. Hao, Y. F. Cai,
L. L. Lin, X. M. Feng* ______ **8644 – 8647**

A Catalytic Asymmetric Ring-Expansion Reaction of Isatins and α-Alkyl-α-Diazoesters: Highly Efficient Synthesis of Functionalized 2-Quinolone Derivatives

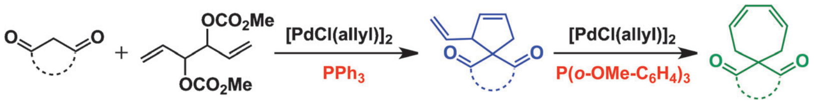


Asymmetric expansion: A catalytic asymmetric ring-expansion reaction of the title compounds occurs in the presence of a $Sc(OTf)_3$ catalyst bearing an *N*,*N*′-dioxide-based ligand. Highly functionalized 2-quinolone derivatives containing a chiral C4-quaternary stereocenter were obtained in high yields and high levels of selectivity under mild reaction conditions (see scheme; Tf = trifluoromethanesulfonyl).

Spiro Compounds

H. Clavier,* L. Giordano,*
A. Tenaglia* ______ **8648 – 8651**

Palladium-Mediated Phosphine-Dependent Chemoselective Bisallylic Alkylation Leading to Spirocarbocycles

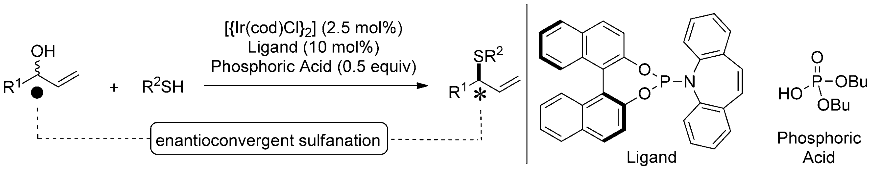


Cycles everywhere: The selectivity in the transformations of 1,3-diones to carbocycles by palladium-catalyzed bisallylic alkylations is strongly dependent on the phosphine that is employed (see scheme). Moreover, synthesized vinylcyclopentenes can be easily transformed into cycloheptadiene derivatives through a carbon–carbon allylic bond cleavage.

Allylic Thioethers

M. Roggen, E. M. Carreira* _ **8652 – 8655**

Enantioselective Allylic Thioetherification: The Effect of Phosphoric Acid Diester on Iridium-Catalyzed Enantioconvergent Transformations

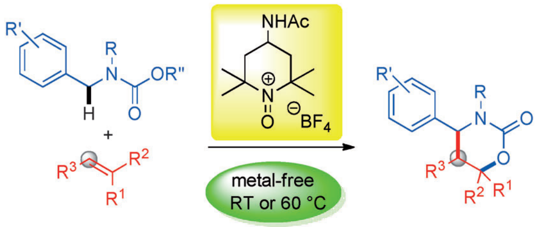


You'll take the high road and I'll take the low road: Enantioenriched allylic thioethers have been synthesized from chiral racemic allylic alcohols. The combination of an Ir–(P,alkene) complex and dibutyl phosphoric acid are required to attain high selectivities. Mechanistic studies uncover an enantioconvergent transformation in which substrate enantiomers react along different pathways to give the same product (see scheme; cod = 1,5-cyclooctadiene).

Synthetic Methods

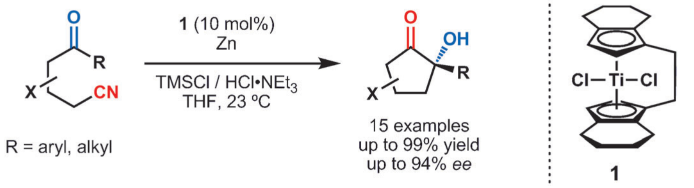
H. Richter, R. Fröhlich, C.-G. Daniliuc,
O. García Mancheño* ______ **8656 – 8660**

Mild Metal-Free Tandem α-Alkylation/Cyclization of *N*-Benzyl Carbamates with Simple Olefins



Easy does it! The chemoselective oxidative α-C(sp^3)–H alkylation/cyclization reaction of *N*-benzyl carbamates using simple mono-, di-, and trisubstituted olefins provides functionalized N-heterocycles such as oxazinones (see picture). A TEMPO oxoammonium salt serves as the oxidant, making it possible to carry out the reaction at low temperatures. Neither a metal catalyst nor preactivation in the α-position to the nitrogen group are needed.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Reduction, please! The title reaction affords α-hydroxyketones, a common structural motif in biologically active natural products, in good yields and high enantioselectivities at room temperature. The commercially available ansa-titanocene **1** was found to be an efficient catalyst for this process, which presumably proceeds by addition of a ketyl radical to a nitrile.

Radical Cyclizations

J. Streuff,* M. Feurer, P. Bichovski, G. Frey, U. Gellrich __________ **8661 – 8664**

Enantioselective Titanium(III)-Catalyzed Reductive Cyclization of Ketonitriles

---

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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

Angewandte Corrigendum

In the Supporting Information for this Communication, the equations S3 and S4 are misprinted. Along with this Corrigendum, a revised Supporting Information is provided. The actual calculations were performed using the correct equations on page S16.
The authors ensure that the changes made in the aforementioned text are only and strictly concerned with literal errors and do not affect any data in the original versions of their Communication and Supporting Information.

Sodium Doping Controlled Synthesis of Monodisperse Lanthanide Oxysulfide Ultrathin Nanoplates Guided by Density Functional Calculations

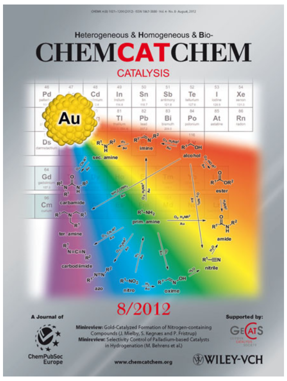
Y. Ding, J. Gu, J. Ke, Y.-W. Zhang,* C.-H. Yan* __________ **12330–12334**

Angew. Chem. Int. Ed. **2011**, *50*

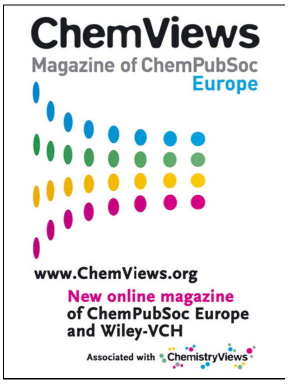
DOI: 10.1002/anie.201105025

Check out these journals:


www.chemasianj.org


www.chemcatchem.org


www.chempluschem.org


www.chemviews.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim