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:

*K. Schober, E. Hartmann, H. Zhang, R. M. Gschwind**
^{1}H DOSY Spectra of Ligands for Highly Enantioselective Reactions—A Fast and Simple NMR Method To Optimize Catalytic Reaction Conditions

*A. M. Scott, A. B. Ricks, M. T. Colvin, M. R. Wasielewski**
Comparing Spin-Selective Charge Transport through Donor–Bridge–Acceptor Molecules having Different Oligomeric Aromatic Bridges

S. Pal, Z. Deng, B. Ding, H. Yan, Y. Liu**
DNA-Origami-Directed Self-Assembly of Discrete Silver Nanoparticle Architectures

*D. Figgen, A. Koers, P. Schwerdtfeger**
NWHClI: A Small and Compact Chiral Molecule with Large Parity Violation Effects in the Vibrational Spectrum

A. M. Nowicka, U. Hasse, G. Sievers, M. Donten, Z. Stojek, S. Fletcher, F. Scholz**
Selective Knock–Out of Active Sites on a Gold Surface

C. Costentin, M. Robert, J. Savéant, C. Tard
Inserting a Hydrogen Bond Relay between Proton Exchanging Sites in Proton–Coupled Electron Transfers

*Q. Liu, G. Li, J. He, J. Liu, P. Li, A. Lei**
Palladium–Catalyzed Aerobic Oxidation and Carbonylation of Arylboronate Esters under Mild Conditions

A. C. Filippou, O. Chernov, K. W. Stumpf, G. Schnakenburg*
Metal–Silicon Triple Bonds: The Molybdenum Silylidyne Complex $[\mathrm{Cp(CO)_2Mo{\equiv}SiR}]$

Author Profile

"My biggest inspiration is the life work of Paul Ehrlich. My favorite subject at school was science, of course ..."
This and more about Carlos F. Barbas III can be found on page 2468.

News

S. Schlücker

G. Schwedt

Obituary

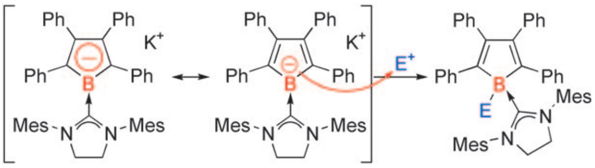
Books

Highlights

Nucleophilic Boron

M. Yamashita* ———— **2474 – 2475**

Nucleophilicity of a Base-Stabilized Borole Anion at the Boron Center



A piece of the π: A nucleophilic carbene-stabilized boryl anion has been prepared by reduction (see scheme). Reactions of this boracycle indicated its nucleophilicity on a π orbital of the central boron atom. The significance of this work is presented along with a background on nucleophilic boron reagents and boracycles.

Active Plasmonics

P. Vasa, C. Lienau* ———— **2476 – 2477**

An Unusual Marriage: Coupling Molecular Excitons to Surface Plasmon Polaritons in Metal Nanostructures

A wavy couple: Hybrid systems that consist of metallic nanostructures and active media, such as semiconductor nanostructures or molecular aggregates, may find interesting applications as nanometer-sized waveguides for light (see picture), ultrafast optical switches, or novel types of nanolasers.

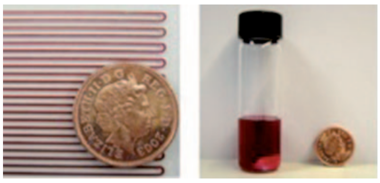
Essays

Process Optimization

F. E. Valera, M. Quaranta, A. Moran, J. Blacker,* A. Armstrong,* J. T. Cabral,* D. G. Blackmond* ———— **2478 – 2485**

The Flow's the Thing...Or Is It? Assessing the Merits of Homogeneous Reactions in Flask and Flow

Against the flow? What factors dictate the relative merits of microflow reactors versus batch-reaction flasks for homogeneous catalytic reactions? The optimal reaction protocol must be decided on a case-by-case basis. Flask reactors equipped with in situ detection devices provide a concise and information-rich means of obtaining the intrinsic kinetic information required to make this decision.



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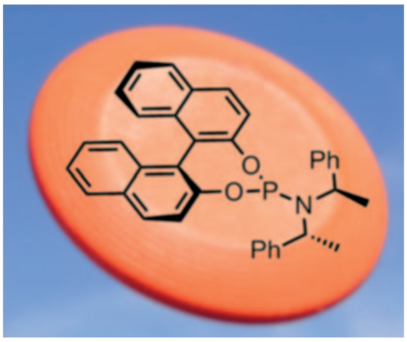
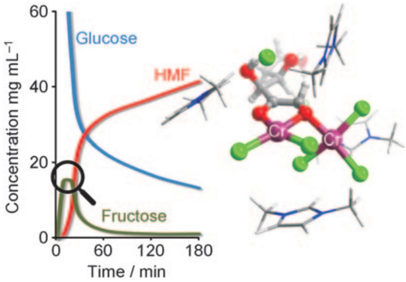
Reviews



A meteoric rise: After their first application in asymmetric conjugate addition reactions in 1996, phosphoramidites have developed into one of the most effective ligands in enantioselective transition-metal catalysis. A particular advantage is their modular synthesis, which allows fine-tuning for a specific catalytic reaction.

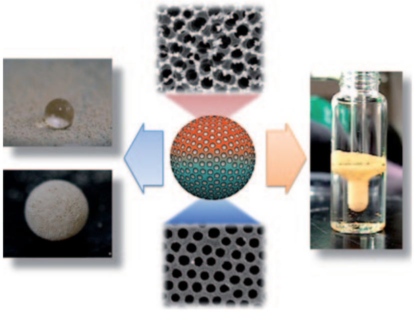
Asymmetric Catalysis

Communications



Cat waiting in the wings: The transient formation of Cr^{2+} dimers through coordination to a second molecule of the catalyst promotes the isomerization of glucose to fructose and explains the unique ability of $CrCl_2$ to catalyze the dehydration of glucose to 5-hydroxymethylfurfural (HMF) in ionic-liquid media. The active-site environment during the rate-controlling step resembles that in hexose isomerase enzymes.

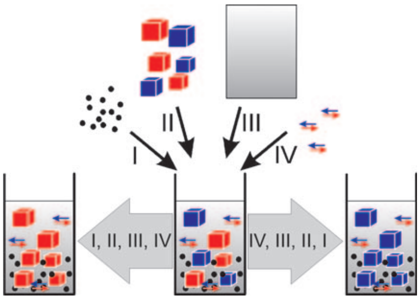
Reaction Mechanisms



Janus microspheres composed of superhydrophobic and hydrophilic hemispherical surfaces were prepared using photocurable Pickering emulsion droplets. Upon placement at an air–water interface, an impregnable superhydrophobic barrier with high flexibility is formed. These microspheres have great potential in size-dependent semipermeable membranes, floating micromachines, and superhydrophobic coatings.

Interfaces

Going forward in reverse: The configuration of the product of grinding-induced symmetry breaking can be controlled simply by the order in which the different reaction-mixture components are combined (see scheme: I) glass beads, II) racemic mixture (enantiomers differentiated by color), III) solvent, IV) racemization catalyst). The underlying mechanism is based on a subtle balance between enantioselective crystal growth and dissolution.



Chiral Resolution

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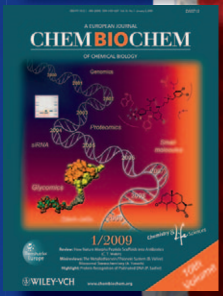

On 21st May 2010 in Paris

at the Maison de la Chimie

(near the Eiffel Tower and Les Invalides)

Speakers


Gerhard Ertl
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


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Michael Grätzel


Michel Orrit


Nicolas Winssinger

Scientific committee

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

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

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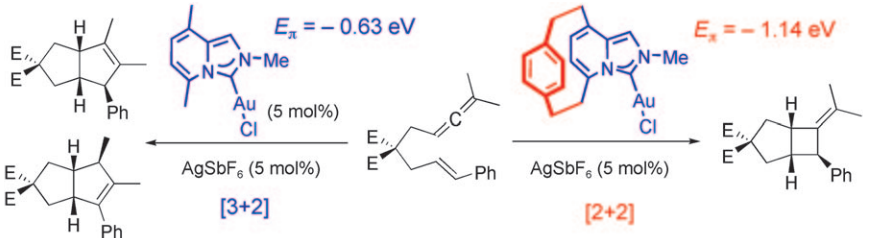

Accept it! Although the π-acceptor properties of N-heterocyclic carbenes (NHCs) are often considered negligible, they can be enhanced to the extent that they start to dominate the catalytic behavior of gold–NHC complexes (see scheme). As it seems to be easier to tune the π acidity of NHCs than to alter their σ-donor properties, the general perception of this important class of ancillary ligands needs to be revised.

Ligand Effects

M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner* ______ **2542 – 2546**

Steering the Surprisingly Modular π-Acceptor Properties of N-Heterocyclic Carbenes: Implications for Gold Catalysis

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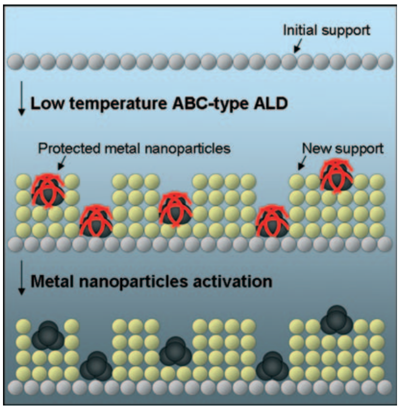

Sheltered growth: A novel atomic layer deposition (ALD) method to synthesize highly uniform ultrafine supported metal nanoparticles is described. The ALD process includes growing protected metal nanoparticles and new support layers simultaneously at low temperature. In the final stage, the activation of the metal nanoparticles can be achieved by removing the protective ligands through calcination or reduction at elevated temperature (see picture).

Deposition Techniques

J. Lu, P. C. Stair* ______ **2547 – 2551**

Low-Temperature ABC-Type Atomic Layer Deposition: Synthesis of Highly Uniform Ultrafine Supported Metal Nanoparticles

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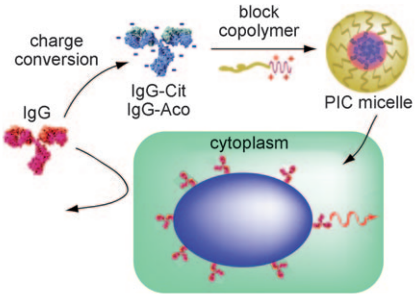

Stand and deliver! Immunoglobulin G (IgG) can be delivered into the cytoplasm of living cells by charge-conversional modification followed by treatment with a cationic block copolymer to form polyion complex (PIC) micelles (see picture). The bioactivity of the IgG selectively recovers in the cell in a pH-dependent manner, thereby controlling the growth of human hepatoma cells through IgG binding to intracellular target molecules.

Antibody Delivery

Y. Lee, T. Ishii, H. J. Kim, N. Nishiyama, Y. Hayakawa, K. Itaka, K. Kataoka* ______ **2552 – 2555**

Efficient Delivery of Bioactive Antibodies into the Cytoplasm of Living Cells by Charge-Conversional Polyion Complex Micelles

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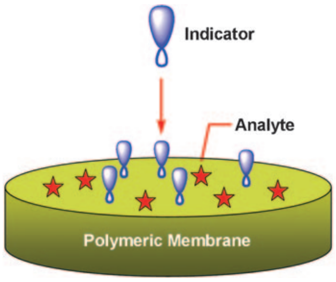


Sensing changes: A uniform-sized molecularly imprinted polymer (MIP), employed as a receptor, can be incorporated into a polymeric membrane used as an ion-selective electrode for the potentiometric sensing of neutral species (see scheme). Changes in the binding sites of the MIP in the membrane phase induced by recognition of the analyte are measured by using an indicator ion that has a molecular structure similar to that of the analyte.

Potentiometric Sensing

R.-N. Liang, D.-A. Song, R.-M. Zhang, W. Qin* ______ **2556 – 2559**

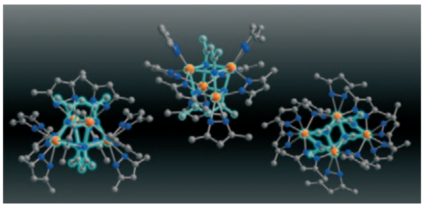
Potentiometric Sensing of Neutral Species Based on a Uniform-Sized Molecularly Imprinted Polymer as a Receptor

Uranium Cluster Chemistry

J. D. Rinehart, S. A. Kozimor,
J. R. Long* ______ 2560 – 2564

Tetranuclear Uranium Clusters by Reductive Cleavage of 3,5-Dimethylpyrazolate

Hard-core uranium chemistry: The 3,5-dimethylpyrazolate anion can be activated by uranium(III) to form 4-ketimidopent-2-ene-2-imido (kipi^{3-}) units, which are isoelectronic to acetylacetonate. Three related tetranuclear uranium cluster compounds were isolated (see picture), of which two are mixed valent.

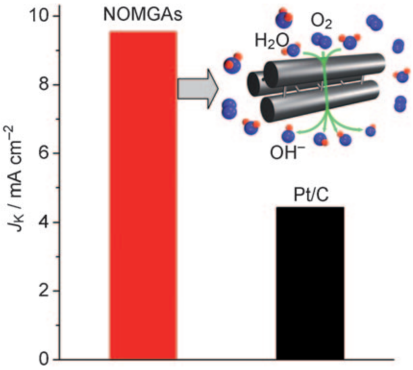


Oxygen-Reduction Catalysts

R. Liu, D. Wu, X. Feng,*
K. Müllen* ______ 2565 – 2569

Nitrogen-Doped Ordered Mesoporous Graphitic Arrays with High Electrocatalytic Activity for Oxygen Reduction

These materials are no dopes: Nitrogen-doped ordered mesoporous graphitic arrays (NOMGAs) prepared by a metal-free procedure exhibited higher electrocatalytic activity than the commercially available Pt–C catalyst (see plot), excellent long-term stability, and resistance to crossover effects in the oxygen-reduction reaction (ORR). Graphite-like nitrogen atoms appear to be responsible for the excellent electrochemical performance in the ORR.

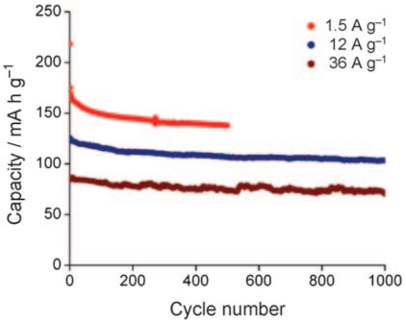


Mesoporous Anodes

Y. Ren, L. J. Hardwick,
P. G. Bruce* ______ 2570 – 2574

Lithium Intercalation into Mesoporous Anatase with an Ordered 3D Pore Structure

Surprising anode material! A mesoporous anatase was synthesized that showed superior rate capability. Even after 1000 charge/discharge cycles at a rate of 12000 mA g^{-1} (1.6 min per cycle), the mesostructure was retained with a stable capacity of 125 mA h g^{-1} (see diagram).

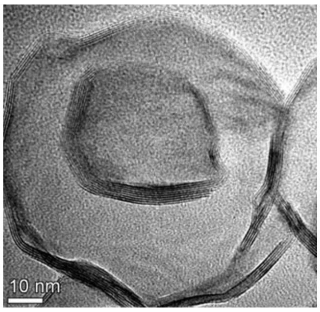


Chalcogenide Fullerenes

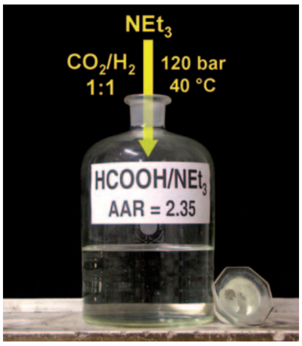
A. Yella, M. Panthöfer, M. Kappl,
W. Tremel* ______ 2575 – 2580

Snapshots of the Formation of Inorganic MoS_2 Onion-Type Fullerenes: A "Shrinking Giant Bubble" Pathway

Growing onions: Formation of onion-type MoS_2 fullerenes was monitored by taking TEM snapshots of reaction intermediates in the thermal decomposition of amorphous precursor particles, which led first to giant multiwall fullerenes ($d > 150$ nm) in which, at higher temperature, smaller daughter fullerenes segregated (see TEM image). Subsequently, tubular nanopods, containing fullerene particles and finally twinned and nested fullerenes, were formed.

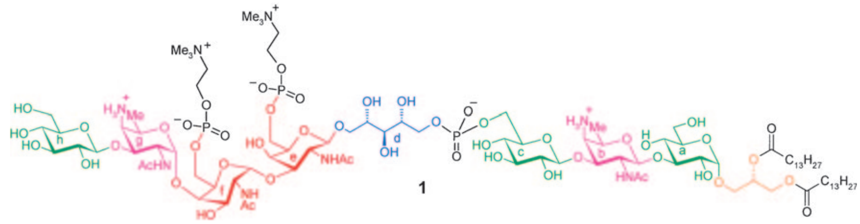


Hydrogen Storage



Adding HCOOH to NEt$_3$ gives a biphasic system of amine and an adduct with a molar acid/amine ratio (AAR) of 1.33. In the presence of a suitable catalyst, CO$_2$/H$_2$ (1:1) acts as HCOOH if both amine and 1.33-adduct phases are present. For example, at 40 °C and 120 bar, neat amine, "doped" with both 1.33 adduct and catalyst, is quantitatively converted into 1.78 adduct, which is distilled as an azeotrope with AAR = 2.35.

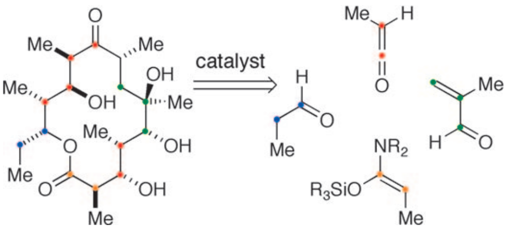
Total Synthesis



1

Mixed signals: The glycophospholipid **1**, consisting of two cholinylphospho-GalNAc units, two 2-acetamino-4-amino-2,4,6-trideoxygalactose rings, three glucose residues each with different linkages to other sugar units, and a ribitolphosphate residue, has been synthesized. Target **1** is recognized by the immune system, but not by the TLR-2 signaling receptor as previously postulated.

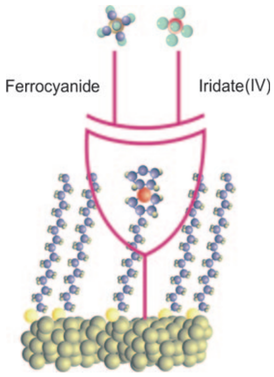
Asymmetric Synthesis



Powerful aldol reactions: Stereoselective Lewis base catalyzed aldol equivalents expediently provided eight of the ten stereocenters required for the synthesis of erythronolide B. Indeed, all eleven stereocenters present in the erythromycin aglycone have been derived directly or indirectly from catalytic asymmetric equivalents of aldol addition reactions (see scheme).

Molecular Logic

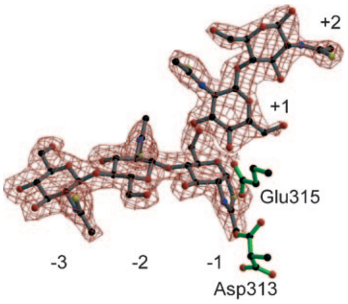
Golden logic: The integration of both cathodic and anodic electrochemical current rectifiers (ECR) on a gold electrode (see picture) results in a molecular-level XOR logic gate with a high switch ratio between electrical output signals "1" and "0". When the electrode is modified by the redox mediator ferrocene, successive XOR logic-gate functions can be carried out without resetting the system.



Enzyme Inhibitors

J. M. Macdonald, C. A. Tarling, E. J. Taylor,
R. J. Dennis, D. S. Myers, S. Knapp,
G. J. Davies, S. G. Withers* . **2599 – 2602**

Chitinase Inhibition by Chitobiose and Chitotriose Thiazolines

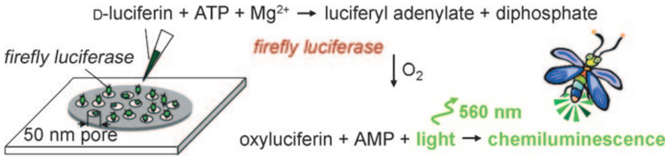


A good imitation: Di- and trisaccharide analogues of the oxazoline intermediate formed during enzymatic hydrolysis of chitin were found to be potent inhibitors of chitinase A. The high affinity and enzymatic stability of a readily synthesized thioamide trisaccharide (two molecules of which are shown in the enzyme active site), and the mechanism-based mode of inhibition, make this analogue a promising candidate for broad-spectrum chitinase inhibition.

Enzyme Detection

S. H. Kang, S. Lee,
E. S. Yeung* **2603 – 2606**

Detection of Single Enzyme Molecules inside Nanopores on the Basis of Chemiluminescence

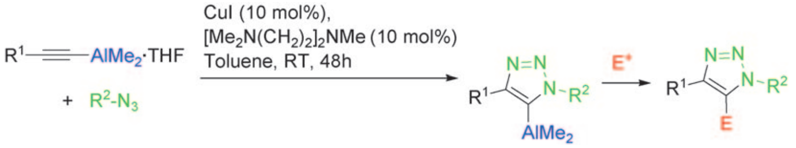


Trapped, but not immobilized inside 50 nm membrane pores, luciferase was detected on the basis of chemiluminescence (see scheme) with an intensified-charge-coupled-device (ICCD) camera. Light emission from the nanopores was concentrated onto individual pixels of the ICCD. Single-molecule detection was possible by integration of the amplified signal over a prolonged enzyme reaction time.

Cycloaddition Reactions

Y. Zhou, T. Lecourt,
L. Micouin* **2607 – 2610**

Direct Synthesis of 1,4-Disubstituted-5-alumino-1,2,3-triazoles: Copper-Catalyzed Cycloaddition of Organic Azides and Mixed Aluminum Acetylides

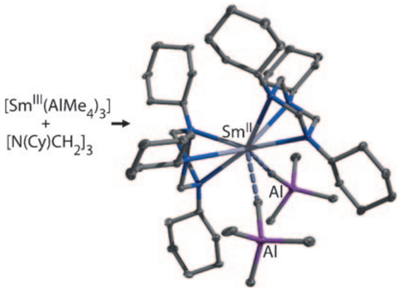


Al together now: Aluminotriazoles are obtained in a fully chemo- and regioselective manner by a copper-catalyzed cycloaddition of organic azides with mixed-aluminum acetylides (see scheme). The carbon–aluminum bond, which is unaffected by the first transformation, is still able to react further with different electrophiles.

Base-Induced Reduction

D. Bojer, A. Venugopal, B. Neumann,
H.-G. Stammler,
N. W. Mitzel* **2611 – 2614**

Lewis Base Induced Reductions in Organolanthanide Chemistry



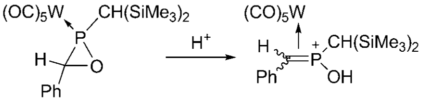
Spontaneous reduction of samarium(III) to samarium(II) is observed upon addition of bulky cyclic triaminals to [Sm(AlMe$_4$)$_3$] (see scheme). The methyl groups of the organometallic precursor act as reductant, and C–H activation is found as a side reaction. This reaction is the first base-induced reduction of a lanthanide(III) complex to lanthanide(II) in the complete absence of stabilizing cyclopentadienyl systems.

Protonation of Oxaphosphiranes

J. Marinas Pérez, H. Helten, B. Donnadieu, C. A. Reed, R. Streubel* ______ 2615 – 2618

Protonation-Induced Rearrangement of an Oxaphosphirane Complex

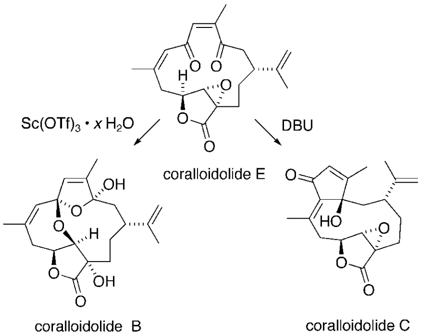
O-Protonation of an oxaphosphirane tungsten complex causes ring opening and the formation of a P–OH functional methylene phosphonium ligand bound side-on to the tungsten center (see scheme).



Biomimetic Synthesis

T. J. Kimbrough, P. A. Roethle, P. Mayer, D. Trauner* ______ 2619 – 2621

Total Synthesis of Coralloidolides A, B, C, and E



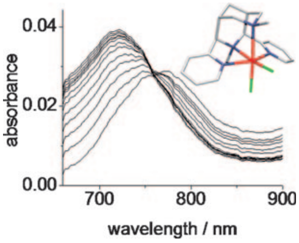
Mapping the matrix: Several coralloidolides, members of a Mediterranean branch of the furanocembranoid family of diterpenes, have been synthesized. The total syntheses include biomimetic transformations that often occur with high chemoselectivity, thus obviating the need for protecting-group manipulations. The fascinating reactivity of 2,5-diene-1,4-dione moieties was explored in detail.

Bioinorganic Enzyme Models

P. Comba,* S. Fukuzumi,* H. Kotani, S. Wunderlich ______ 2622 – 2625

Electron-Transfer Properties of an Efficient Nonheme Iron Oxidation Catalyst with a Tetradentate Bispidine Ligand

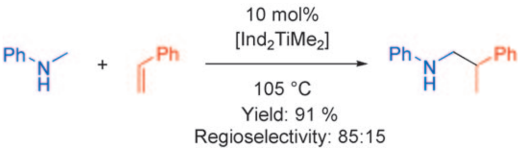
The oxidation catalyst [(L)Fe^{IV}=O] (see picture; L is a tetradentate bispidine ligand) has the highest known one-electron reduction potential for a Fe^{IV}=O species (0.73 V vs. SCE). Investigations into the electron-transfer kinetics show a linear correlation with the bond dissociation energy of the organic substrates.



Titanium Catalysis

R. Kubiak, I. Prochnow, S. Doye* ______ 2626 – 2629

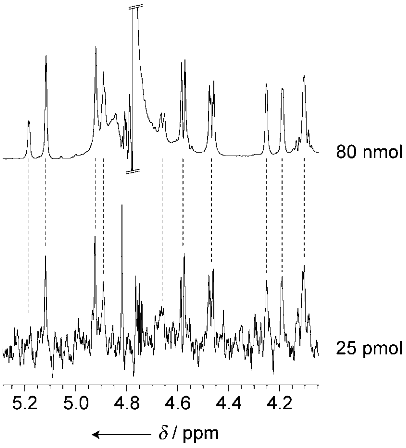
[Ind$_2$TiMe$_2$]: A Catalyst for the Hydroaminomethylation of Alkenes and Styrenes



Metal-catalyzed hydroaminomethylations of styrenes, which take place by C–H bond activation, can be achieved in the presence of the catalyst [Ind$_2$TiMe$_2$] (Ind = η^5-indenyl). Corresponding reactions of 1-alkenes with *N*-methylanilines performed at temperatures between 80 °C and 105 °C usually take place with regioselectivities of better than 99:1 in favor of the branched product.

Contents

Ultrasensitive NMR Spectroscopy



Can you see it? NMR spectroscopy is indispensible for structure analysis. It is believed that its use is limited if less than several nanomoles are available. The characterization of oligosaccharides as components of glycoproteins by NMR spectroscopy utilizing significantly less material is highly desirable. Optimization of the sample preparation, water suppression, and instrument setup has enabled only 15 picomoles of oligosaccharides to be analyzed by NMR spectroscopy.

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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