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:

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α-Amino Acids

*T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov**
Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety

*W. Xu, X. Xue, T. Li, H. Zeng, X. Liu**
Ultrasensitive and Selective Colorimetric DNA Detection by Nicking Endonuclease-Assisted Nanoparticle Amplification

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama, H. Tokuyama**
Total Synthesis of (+)-Haplophytine

G. A. Zelada, J. Riu, A. Düzgün, F. X. Rius**
Immediate Detection of Living Bacteria at Ultra-Low Concentrations Using a Carbon-Nanotube-Based Potentiometric Aptasensor

*K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama**
Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

A. Giannis, P. Heretsch, V. Sarli, A. Stößel*
Synthesis of Cyclopamine Using a Biomimetic and Diastereoselective Approach

Author Profile

"My favorite subject at school was soccer. When I was eighteen I wanted to be a scientist.. …"
This and more about Yitzhak Apeloig can be found on page 6584.

News

Science Forum of the German Chemical Society

G. Erker

P. Knochel

W. Leitner

C. Strohmann

M. Veith

Books

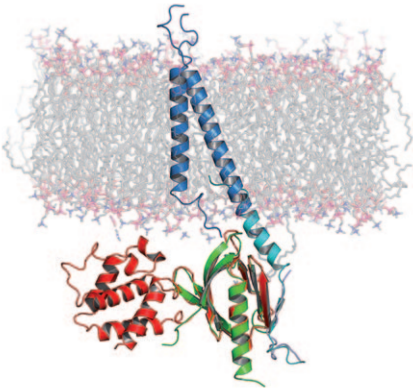
Contents

Highlights

Signal Transduction

M. Hoefling, H. Kessler,
K.-E. Gottschalk* ——— **6590 – 6593**

The Transmembrane Structure of Integrin αIIbβ3: Significance for Signal Transduction

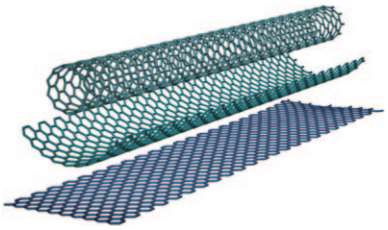


Outside contact: Cells in multicellular organisms regulate their adhesion through specialized integrin receptors, which relay signals bidirectionally between the inside and outside of cells. The transmembrane domains (see picture, blue; the integrin–talin complex is red and green) of integrins are the center of the signaling process. Recently, structures of these domains have been reported that shed light on the signal transduction mechanism.

Carbon Nanoribbons

A. Hirsch* ——— **6594 – 6596**

Unzipping Carbon Nanotubes: A Peeling Method for the Formation of Graphene Nanoribbons

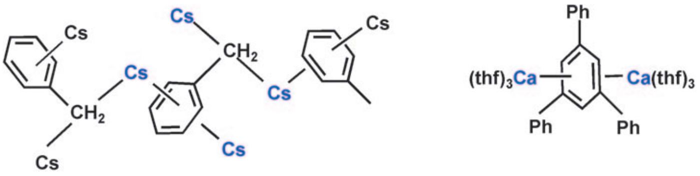


Zipper examined: Elegant unzipping procedures result in the clean opening of multiwalled carbon nanotubes, leading to graphene nanoribbons (see scheme). Since graphene exhibits outstanding electronic properties, this method may be important in the development of modern nanoelectronic applications.

Coordination Modes

J. D. Smith* ——— **6597 – 6599**

Organometallic Compounds of the Heavier s-Block Elements—What Next?



Getting heavy: A novel dicesium methandiide and an organometallic compound of Ca^{I} without a Ca–Ca bond (see picture) are examples of species in which metals coordinate to anions. Thus, the normal statement that "ligands coordinate to metals" must be reversed.

For the USA and Canada:
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Essays

Wilhelm Ostwald

A great researcher, Wilhelm Ostwald, is honored here on the occasion of the hundredth anniversary of his receiving the Nobel Prize. At the time of the award in December 1909 he said that he was surprised that this highest scientific distinction was awarded for his work on catalysis; he expected that such recognition would come much later.

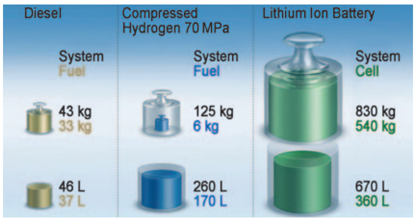
WILHELM
OSTWALD

såsom ett erkännande åt hans arbeten öfver katalys jämte hans härför grundläggande undersökningar öfver kemiska jämviktsförhållanden och reaktionshastigheter.

Reviews

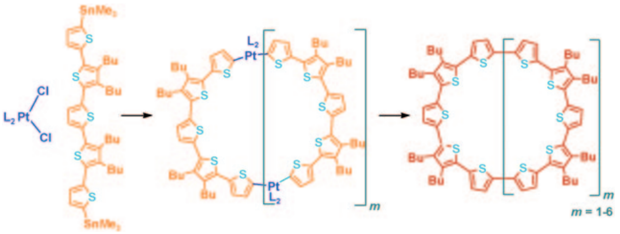
Hydrogen Storage

The stuff dreams are made of: Hydrogen is a promising energy carrier in future energy systems, but the storage for mobile and stationary applications is a substantial challenge. If on-board hydrogen storage of car running on a fuel cell can be solved, then also the other problems of a hydrogen infrastructure appear to be manageable. The picture compares the weight and volume of various fuels and tank systems for vehicles having a 500 km range.

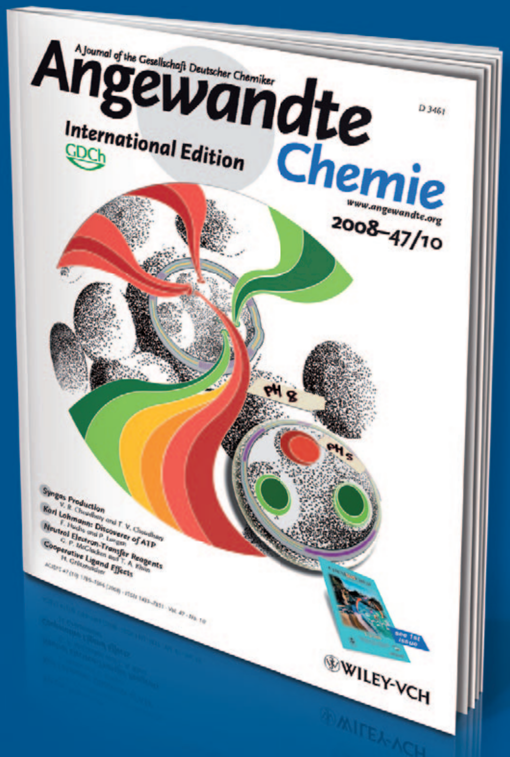


Communications

Conjugated Macrocycles



Dual roles and nanorings: A new family of cyclic oligothiophenes with up to 35 thiophene units is synthesized by using platinum complexes in a dual role as template and as reactive center. The ease of ionization and aggregation of the new compounds indicates that they have promising properties for use as organic electronic materials of increased structural complexity.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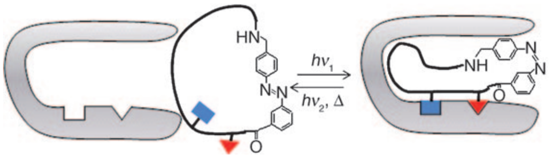


Lit-up β attracts α: An azobenzene-ω-amino acid is incorporated as a photoswitch into a β-hairpin motif that mimics the binding site in neuronal NO synthase for α-syntrophin. Light-induced isomerization reversibly converts the stable monomer model peptide from its nonbinding, nonstructured *trans* form into the β-sheet-forming *cis* form which shows a remarkable affinity for α-syntrophin.

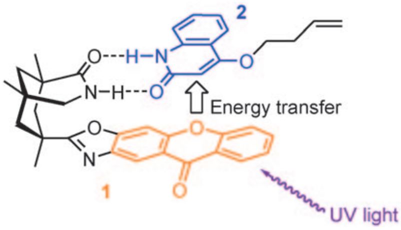
Biphotonics

C. Hoppmann, S. Seedorff, A. Richter,
H. Fabian, P. Schmieder, K. Rück-Braun,*
M. Beyermann* ———— **6636 – 6639**

Light-Directed Protein Binding of a Biologically Relevant β-Sheet

---

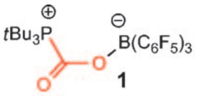
Collection, sensitization, and selection are the tasks of the organocatalyst **1**, which it fulfills almost perfectly in the photochemical conversion of quinolone **2**. It collects light ($\lambda > 350$ nm), transfers its energy to the substrate, and induces a high enantioselectivity. Even with only 10 mol% of catalyst, a yield of 90% was achieved with an *ee* value of 92%.



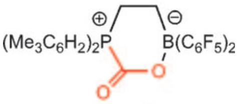
Photochemistry

C. Müller, A. Bauer, T. Bach* **6640 – 6642**

Light-Driven Enantioselective Organocatalysis



1



2

Hot and bothered? Frustrated Lewis pairs comprising phosphine and borane react to reversibly bind and release CO_2, offering a rare example of metal-free CO_2 sequestration. The mechanism of formation of these CO_2 derivatives **1** and **2** (see scheme) by almost simultaneous P–C and O–B bond formation was characterized by quantum chemical calculations.

CO_2 Binding

C. M. Mömming, E. Otten, G. Kehr,
R. Fröhlich, S. Grimme,* D. W. Stephan,*
G. Erker* ———— **6643 – 6646**

Reversible Metal-Free Carbon Dioxide Binding by Frustrated Lewis Pairs

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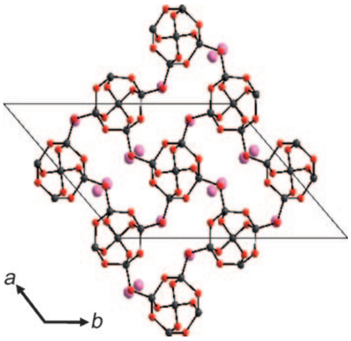


No gas too small: A synthetic potassium gallosilicate natrolite with Si/Ga = 1.28 (denoted PST-1; see picture, Ga/Si gray, O red, K pink) was found to selectively adsorb small gases, especially H_2, and hence to discriminate them from slightly larger molecules such as Ar or CO_2. The remarkable ease of its dehydration and great (hydro)thermal stability make PST-1 a potential candidate for fast, selective H_2 or He separation processes.

Gas Separation

J. Shin, M. A. Camblor, H. C. Woo,
S. R. Miller, P. A. Wright,
S. B. Hong* ———— **6647 – 6649**

PST-1: A Synthetic Small-Pore Zeolite that Selectively Adsorbs H_2

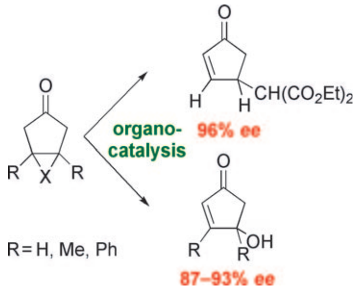
Contents

Asymmetric Synthesis

G. Dickmeiss, V. De Sio, J. Udmark,
T. B. Poulsen, V. Marcos,
K. A. Jørgensen* ________ **6650 – 6653**

Organocatalytic Asymmetric Desymmetrization–Fragmentation of Cyclic Ketones

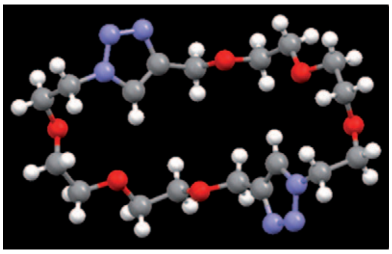
A ticket to total synthesis: The title reaction of *meso* cyclopropane cyclopentanones and epoxycyclopentanones was catalyzed by thiourea-containing cinchona alkaloids with good to excellent enantioselectivity (see scheme). The concept was extended to a one-pot asymmetric desymmetrization–fragmentation–Michael addition by including a nucleophile. A kinetic resolution based on this method was also demonstrated.



Macrocycles

S. Binauld, C. J. Hawker, E. Fleury,
E. Drockenmuller* ________ **6654 – 6658**

A Modular Approach to Functionalized and Expanded Crown Ether Based Macrocycles Using Click Chemistry

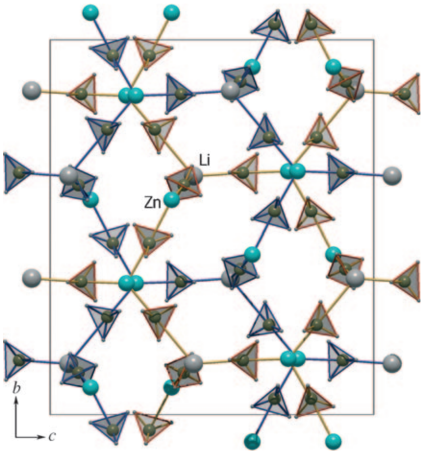


Tailored handcuffs: α-Azide-ω-alkyne oligomers are obtained in high yields from copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC), iterative chain growth, and protection–deprotection strategies. Intramolecular CuAAC under pseudo-high-dilution conditions then yields macrocycles with $n = 1$–8 triazole units in the cyclic backbone (picture shows $n = 2$; C gray, O red, N blue, H white).

Hydrogen Storage

D. Ravnsbæk, Y. Filinchuk,* Y. Cerenius,
H. J. Jakobsen, F. Besenbacher,
J. Skibsted, T. R. Jensen* ____ **6659 – 6663**

A Series of Mixed-Metal Borohydrides

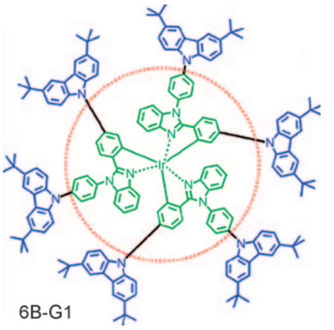


Mix and match: A novel series of alkali-metal zinc borohydrides, $LiZn_2(BH_4)_5$ (see picture), $NaZn_2(BH_4)_5$, and $NaZn(BH_4)_3$, with fascinating structures are presented. An interpenetrated network structure, containing a $[Zn_2(BH_4)_5]^-$ ion, is observed for the first time for a borohydride. A three-dimensional framework containing a polymeric $[\{Zn(BH_4)_3\}_n]^{n-}$ ion is also identified.

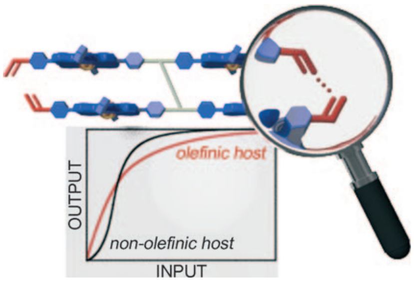
Dendrimers

J. Ding, B. Wang, Z. Yue, B. Yao, Z. Xie,
Y. Cheng, L. Wang,* X. Jing,
F. Wang ________ **6664 – 6666**

Bifunctional Green Iridium Dendrimers with a "Self-Host" Feature for Highly Efficient Nondoped Electrophosphorescent Devices



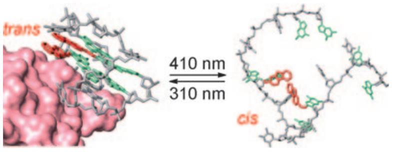
Better without doping: Use of a dendron with a high carbazole density around an iridium core has been found to improve the performance of nondoped electrophosphorescent devices more effectively than the use of higher-generation dendrimers. A promising efficiency as high as 45.7 cd A^{-1} (13.4 %) together with a high luminance is obtained for 6 B-G1 (see picture). These values are very close to those of the corresponding doped device.



Super sensitive: A new method based on the guest-binding behavior of allosteric host molecules has been used to sensitively detect a weak olefin–olefin interaction with high precision (see picture).

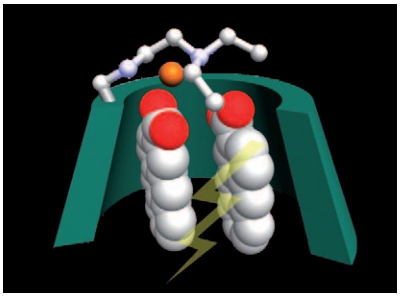
Olefin Detection

Getting a grip: G-quadruplex formation can be regulated by reversible *cis–trans* photoisomerization of the photochromic nucleobase 8-fluorenylvinyl-2′-deoxyguanosine (see picture: fluorene red, guanine green). Switching between a very stable quadruplex state and a non-structured state allows controlled binding to thrombin (pink).

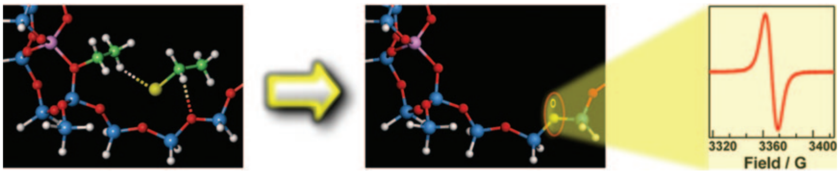


DNA Conformational Switches

Cap in hand: Combined use of diamino-γ-cyclodextrin (CD) and $Cu(ClO_4)_2$ resulted in the first catalytic supramolecular photochirogenesis in the photocyclodimerization of 2-anthracenecarboxylic acid. The *anti*-head-to-head cyclodimer formed in 64–70% enantiomeric excess and about 50% yield; these values are the highest ever reported for CD-mediated photochirogenesis.

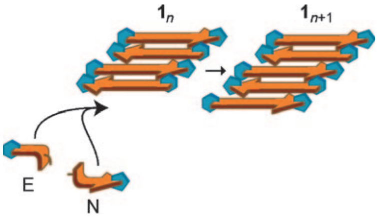


Photochirogenesis



Making a hole: Oxygen atoms bridging two silicon atoms in a protonated zeolite can be oxidized through reaction with an alkyl bromide to generate paramagnetic centers in the zeolite framework (see structures and EPR spectrum; red O, blue Si, purple Al, green C, yellow Br, white H). Electron transfer from the zeolite framework could partially explain the range of products formed in acid-catalyzed reactions with zeolite catalysts.

Redox Sites in Zeolites



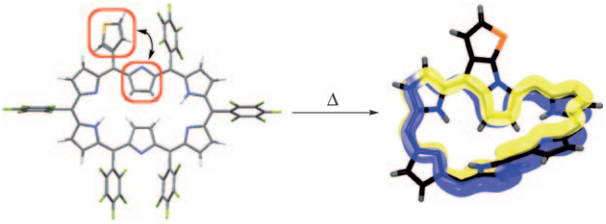
Simple peptides can do that too: Synthetic amphiphilic peptides **1**, formed of electrophilic (E) and nucleophilic (N) precursors, are close analogues of the Glu-(Phe-Glu)$_n$ molecules. The peptides form soluble one-dimensional β-sheet aggregates in water (see picture), and serve to significantly accelerate chemical ligation and self-replication.

Synthetic Replicators

Möbius Aromaticity

M. Inoue, K. S. Kim, M. Suzuki, J. M. Lim,
J.-Y. Shin, D. Kim,*
A. Osuka* ________________ **6687 – 6690**

Thermal Fusion Reactions of *meso*-(3-Thienyl) Groups in [26]Hexaphyrins to Produce Möbius Aromatic Molecules



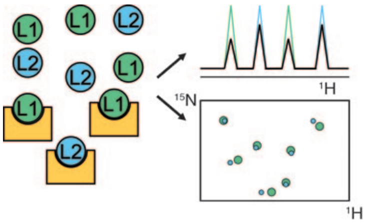
Fuse to twist: Simple thermal reactions of *meso*-(3-thienyl) groups in Hückel-aromatic [26]hexaphyrins (see picture, left; N blue, S yellow, F green) provide 3-thienyl-fused [28]hexaphyrins (right) that have Möbius aromatic character, as indicated by a number of spectroscopic methods.

Binding Affinity

X. Zhang, A. Sänger, R. Hemmig,
W. Jahnke* ________________ **6691 – 6694**

Ranking of High-Affinity Ligands by NMR Spectroscopy

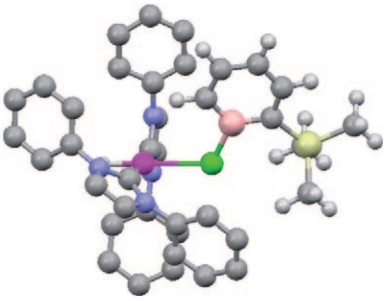
Let the protein choose its ligand, and use NMR spectroscopy to see which one it has chosen (see scheme). This principle enables the most precise determination of relative binding affinities of two ligands to a protein receptor and for the first time allows the affinities of tightly binding ligands to be determined by NMR spectroscopy. This approach is a valuable tool for the lead-optimization process.



Lewis Acid Adducts

A. Languérand, S. S. Barnes,
G. Bélanger-Chabot, L. Maron,
P. Berrouard, P. Audet,
F.-G. Fontaine* ________________ **6695 – 6698**

[(IMes)$_2$Pt(H)(ClBC$_5$H$_4$SiMe$_3$)]: a Borabenzene–Platinum Adduct with an Unusual Pt-Cl-B Interaction

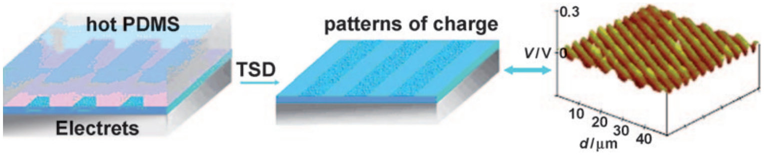


A Pt-Cl-B interaction is observed when a borabenzene derivative reacts with a platinum(0) precursor with bulky N-heterocyclic carbene ligands. The resulting platinum(II) complex (see picture; Pt red, N blue, Cl green, B pink, Si yellow) involves a new bonding mode for borabenzene, which usually binds in an η^6 fashion to transition metals.

Electrets

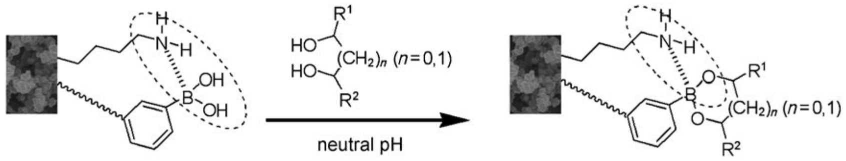
D. Zhao, L. Duan, M. Xue, W. Ni,
T. Cao* ________________ **6699 – 6703**

Patterning of Electrostatic Charge on Electrets Using Hot Microcontact Printing



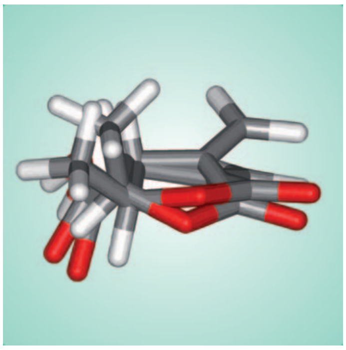
Stamp on a hot tin roof: A topographically patterned poly(dimethylsiloxane) (PDMS) stamp is heated to 50–220 °C. This stamp uses the heat energy as "ink" for microcontact printing (µCP) by inducing chemical cross-linking, decomposition, or other transformations. The hot µCP technique can pattern electrostatic charges on electrets by selective thermally stimulated discharge (TSD, see picture) or depolarization.

Monolithic Materials



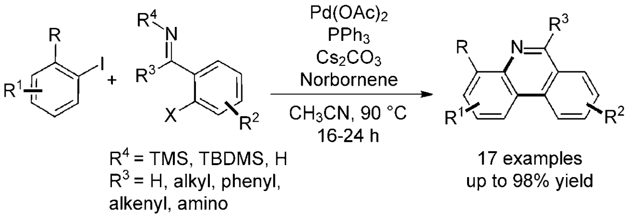
Molecular teamwork: Synergistic co-monomers contained in a boronate-functionalized polymeric monolith function as a single Wulff-type boronic acid ligand to enable the specific capture of *cis*-diol-containing biomolecules under neutral conditions (see scheme). When the medium is made more acidic, the amine group is protonated, and B–N coordination is broken, which results in the release of the *cis* diol from the monolith.

NMR Spectroscopy



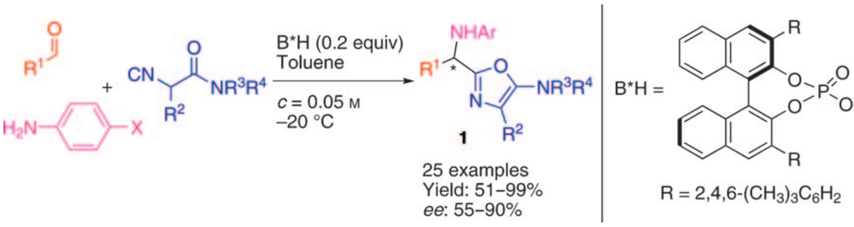
Mission possible! The motional averaging of NMR spectroscopic data complicates the determination of conformation and relative configuration in flexible organic molecules. Two alternative routes are discussed for the treatment of conformational equilibrium in a moderately flexible compound (see the superposition of the two conformers of the butyrolactone studied) when residual dipolar couplings are used.

Domino Reactions



Domino reactions possess the ability to generate complexity from simple starting materials. Disclosed is a strategy for the domino direct arylation/N-arylation for the facile construction of diverse phenanthridine derivatives (see scheme; TMS = trimethylsilyl, TBDMS = *tert*-butyldimethylsilyl).

Multicomponent Reactions



All three together now: Three-component reactions of aldehydes, anilines, and α-isocyanoacetamides in the presence of a catalytic amount of chiral phosphoric acid afforded the 5-(1-aminoalkyl)-5-aminooxazole **1** in excellent yields and moderate to good enantiomeric excess (see scheme).

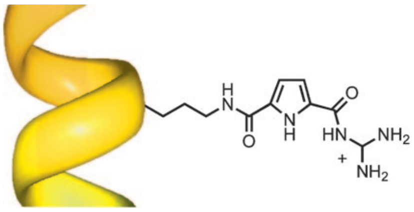
Contents

Enzyme Mimics

N. J. V. Lindgren, L. Geiger, J. Razkin, C. Schmuck,* L. Baltzer* ___ **6722 – 6725**

Downsizing of Enzymes by Chemical Methods: Arginine Mimics with Low pK_a Values Increase the Rates of Hydrolysis of RNA Model Compounds

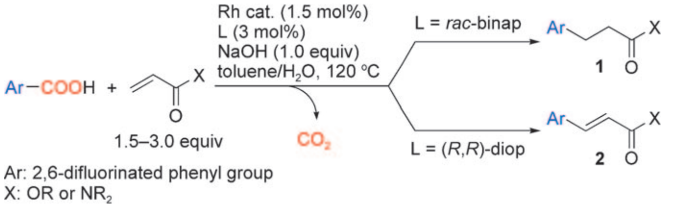
A talented mimic: Large rate enhancements were observed in the catalysis of reactions of RNA models when two arginine residues and two histidine residues were replaced with residues with a guanidiniocarbonyl pyrrole (Gcp) side chain (see structure) in a folded polypeptide catalyst. Gcp fulfilled the functions of, and even outperformed, both Arg and His.



Synthetic Methods

Z.-M. Sun, P. Zhao* ___ **6726 – 6730**

Rhodium-Mediated Decarboxylative Conjugate Addition of Fluorinated Benzoic Acids: Stoichiometric and Catalytic Transformations

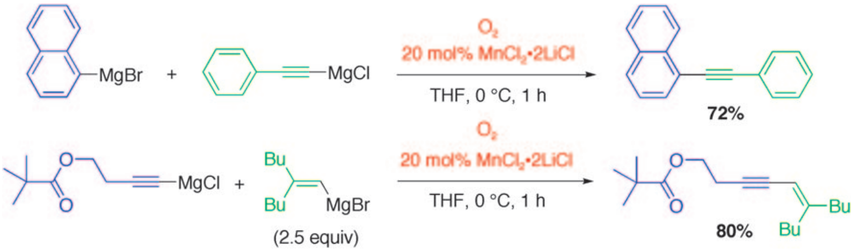


Depending on the bisphosphine ligand, the decarboxylation of 2,6-difluorinated benzoic acids with a Rh^I catalyst in the presence of an acrylic ester or acrylamide led preferentially to conjugate addition (product **1**) or Heck–Mizoroki arylation (product **2**; binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, diop = 4,5-bis(diphenylphosphanylmethyl)-2,2-dimethyl-1,3-dioxolane).

Cross-Coupling

G. Cahiez,* C. Duplais, J. Buendia ___ **6731 – 6734**

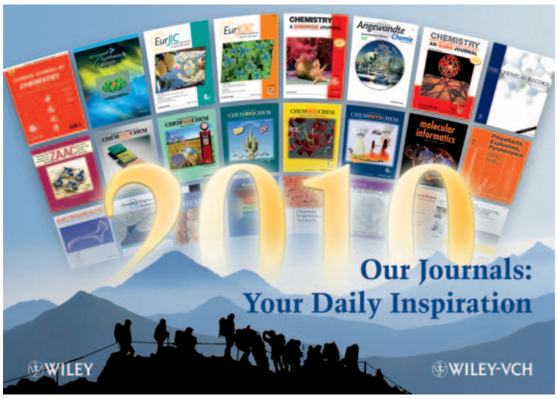
Manganese-Catalyzed Oxidative Cross-Coupling of Grignard Reagents with Oxygen as an Oxidant



Oxidative heterocoupling between two Grignard reagents RMgX and R′MgX is made possible by manganese catalysis with O_2 as an oxidant. This procedure, development of which was based on mechanistic analysis of the corresponding homocoupling reaction, can be steered towards the heterocoupling product at the expense of the homocoupling products by judicious choice of the R and R′ groups (see examples).

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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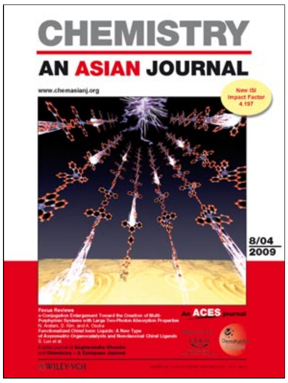

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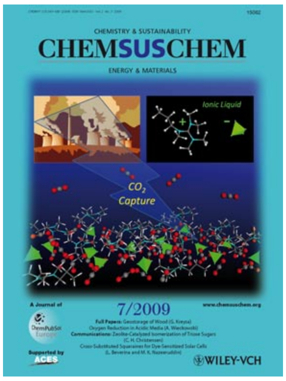

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