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:

*T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey**
Preparation of a Dihydrogen Complex of Cobalt

*Y. Matsuki, M. T. Eddy, R. G. Griffin, J. Herzfeld**
Rapid 3D MAS NMR Spectroscopy at Critical Sensitivity

Z. Zhao, E. L. Jacovetty, Y. Liu, H. Yan**
Encapsulation of Gold Nanoparticles in a DNA-Origami Cage

M. Barsukova-Stuckart, N. V. Izarova, G. B. Jameson, V. Ramachandran, Z. Wang, J. van Tol, N. S. Dalal, R. N. Biboum, B. Keita, L. Nadjo, U. Kortz**
The Dicopper(II)-Containing 22-Palladate(II) $[Cu^{II}_2Pd^{II}_{22}P^{V}_{12}O_{60}(OH)_8]^{20-}$

F. Liao, Y. Huang, J. Ge, W. Zheng, K. Tedsree, P. Collier, X. Hong, S. C. Tsang**
Morphology-Dependent Interactions of ZnO with Cu Nanoparticles at the Materials Interface in the Selective Hydrogenation of CO_2 to CH_3OH

R. Langer, G. Leitus, Y. Ben-David, D. Milstein
Efficient Hydrogenation of Ketones Catalyzed by an Iron Pincer Complex

J. Vogelsang, J. Brazard, T. Adachi, J. C. Bolinger, P. F. Barbara*
Watching the Annealing Process One Polymer Chain at a Time

*H. Ishikawa, M. Honma, Y. Hayashi**
One-Pot Synthesis of a DPP4 Inhibitor by a Four-Component Coupling Reaction Mediated by Diphenylprolinol Silyl Ether

*Z. Liutkevičiūtė, E. Kriukienė, I. Grigaitytė, V. Masevičius, S. Klimašauskas**
Methyltransferase-Directed Derivatization of 5-Hydroxymethylcytosine in DNA

A. Corma, O. de la Torre, M. Renz, N. Villandier*
Production of High-Quality Diesel from Biomass Waste Products

Author Profile

“My favorite subjects at school were history and mathematics. When I was eighteen I wanted to be Professor in a scientific field. …”
This and more about Didier Astruc can be found on page 1750.

News


T. Ritter


C.D. Vanderwal


S. J. Cheon

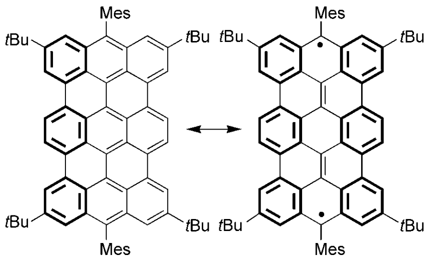
Books

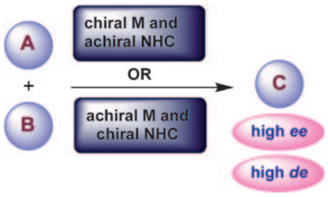
© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Contents

Highlights

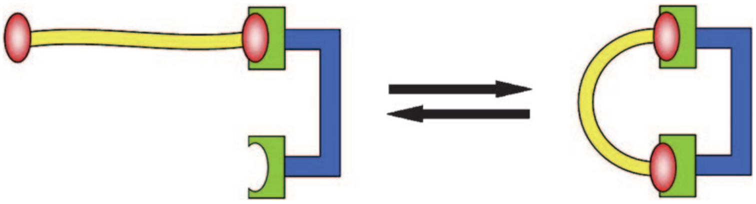
Teranthene—a molecular section of graphene: The surprising stability of teranthene at ambient conditions allowed its characterization, which pointed toward a high biradical contribution in the singlet ground state (see scheme). Polycyclic aromatic hydrocarbons with high singlet biradical character show high third-order nonlinear optical properties, which makes them interesting candidates for (opto)-electronic devices.





A co-op: Recent examples on cooperative catalysis, involving metals (M) and N-heterocyclic carbenes (NHCs), delivered products with high enantioselectivity (see scheme). Such products are not possible to obtain by using either of the catalysts individually.

Essays

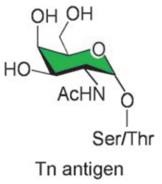


Vive la différence: The distinction between different types of cooperativity is essential for understanding the fundamentals involved. The three title cooperative effects arise from the interplay of intermolecular binding interactions, the presence of one or more intramolecular binding interactions, and, in the latter case, their possible interplay. A master equation for the stability of an assembly is outlined that takes into account all of the three possible types of cooperativity.

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$ 9442/8583 (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.

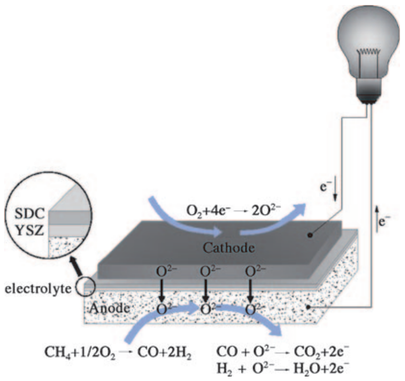
Reviews

An abnormal sugar: The expression of the abnormal *O*-glycan called Tn antigen (see structure) in animal glycoproteins typically represents a disease condition. This Review discusses a broad range of chemical and biological studies on the Tn antigen that could lead to new diagnostics and therapeutics.

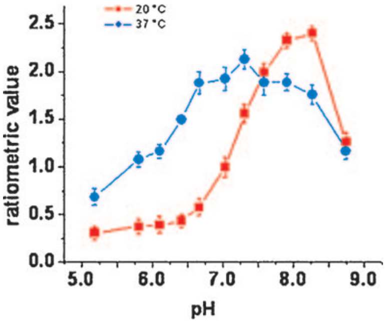


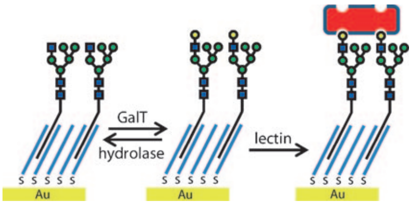
Communications

A harmonic generator: Co-generation of electric power and synthesis gas from methane is achieved using a single-chamber solid oxide fuel cell (see picture; SDC = samarium-doped ceria, YSZ = yttrium-stabilized zirconia). The process utilizes methane completely with zero greenhouse gas emissions.



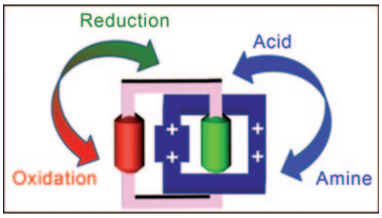
A multiple response: Yb^{III}-HPDO3A has been used for the development of a magnetic resonance imaging method that is able to assess pH value and temperature simultaneously, irrespective of the concentration of the complex (see graph). This contrast agent has potential in a clinical setting as it shows the same stability and in vivo pharmacokinetic properties as Gd^{III}-HPDO3A, which is already used in clinical practices under the trade name of ProHance.

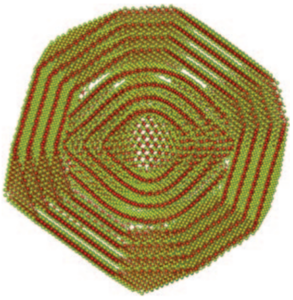


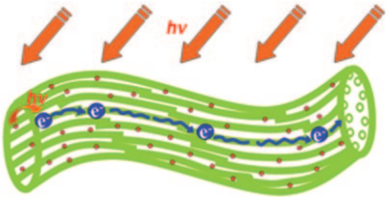


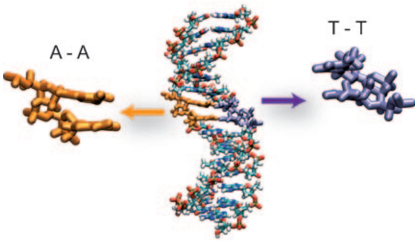
Active arrays: Complex lipid-tagged oligosaccharides, including large multi-antennary species, can be efficiently immobilized on self-assembled monolayers of alkyl mercaptans (see picture). These arrays can be used to follow the action of a galactosyltransferase (GalT) and a hydrolase. The utility of the system for the selective trapping and identification of a lectin from a complex mixture was also demonstrated.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim


Reduction
Acid
Oxidation
Amine




hν

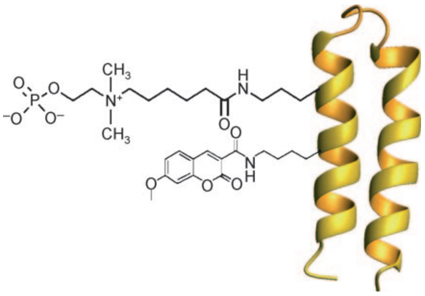

A - A
T - T

Small-Molecule Binders

L. T. Tegler, G. Nonglaton, F. Büttner, K. Caldwell, T. Christopeit, U. H. Danielson, K. Fromell, T. Gossas, A. Larsson, P. Longati, T. Norberg, R. Ramapanicker, J. Rydberg, L. Baltzer* ______ 1823 – 1827

Powerful Protein Binders from Designed Polypeptides and Small Organic Molecules—A General Concept for Protein Recognition

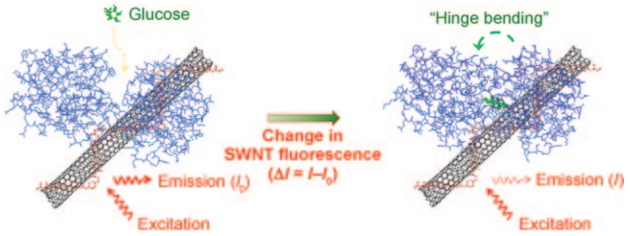
High-affinity binders for the C-reactive protein (CRP), with dissociation constants in the pM to nM range and selectivities in human serum comparable to those of antibodies, were obtained by conjugation of 16 designed polypeptides to phosphocholine, a small molecule that binds CRP with a K_D value of 5 μM (see picture). The polypeptides were not designed specifically to recognize CRP and bind by an adapted fit mechanism.



Bioanalytical Sensors

H. Yoon, J.-H. Ahn, P. W. Barone, K. Yum, R. Sharma, A. A. Boghossian, J.-H. Han, M. S. Strano* ______ 1828 – 1831

Periplasmic Binding Proteins as Optical Modulators of Single-Walled Carbon Nanotube Fluorescence: Amplifying a Nanoscale Actuator



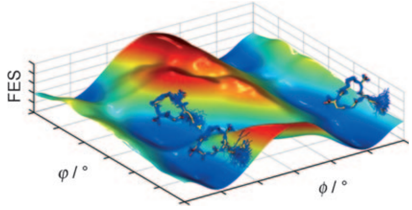
Glucose sensor: Glucose-binding protein (GBP) covalently conjugated to a fluorescent single-walled carbon nanotube (SWNT) is shown to act as an optical switch. Hinge-bending response to glucose causes a reversible exciton quenching of the SWNT fluorescence with high selectivity (see scheme).

Molecular Dynamics

A. Spitaleri, M. Ghitti, S. Mari, L. Alberici, C. Traversari, G.-P. Rizzardi,* G. Musco* ______ 1832 – 1836

Use of Metadynamics in the Design of isoDGR-Based αvβ3 Antagonists To Fine-Tune the Conformational Ensemble

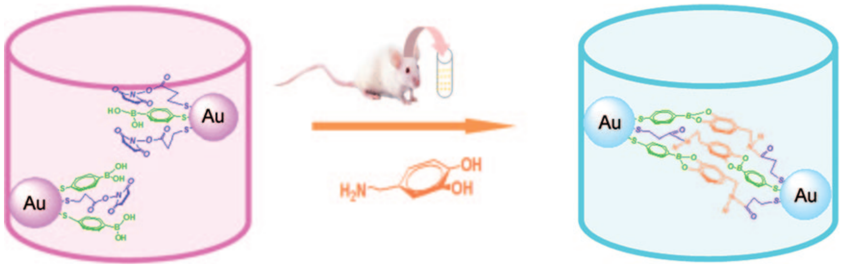
A pretty pair: Metadynamics/docking proved itself as an innovative technique combination to improve the rational design of diagnostic and therapeutic agents based on the isoDGR motif (see picture; FES = free-energy surface). The coupling of these techniques might be exploited for other ligand–receptor systems following the identification of appropriate collective variables for the characterization of ligand conformational ensembles.



Colorimetric Visualization

B. Kong, A. Zhu, Y. Luo, Y. Tian,* Y. Yu, G. Shi ______ 1837 – 1840

Sensitive and Selective Colorimetric Visualization of Cerebral Dopamine Based on Double Molecular Recognition



Seeing is believing: A direct, selective, and sensitive strategy for colorimetric visualization of cerebral dopamine has been developed for the first time using gold nanoparticles through the design of double molecular recognition (see picture). The simplicity of this method establishes a facile and reliable approach for monitoring cerebral species in brain chemistry, which may be related to physiological and pathological events.

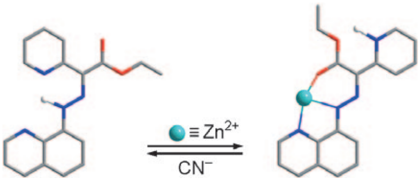
© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Contents

Biomimetic Switches

X. Su, T. F. Robbins,
I. Aprahamian* **1841 – 1844**

Switching through Coordination-Coupled Proton Transfer

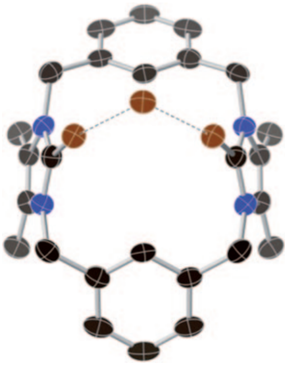


Hold the protons! A hydrazone-based rotary switch underwent *E*/*Z* isomerization upon treatment with Zn^{2+} (see picture) through coordination-coupled proton transfer by a mechanism inspired by biological processes that take place in the reaction centers of photosynthetic bacteria and in cation-diffusion facilitators. The process is fully reversible, as the initial *E* configuration can be reinstated by treatment of the zinc complex with cyanide.

Anion Recognition

A. Caballero, N. G. White,
P. D. Beer* **1845 – 1848**

A Bidentate Halogen-Bonding Bromoimidazoliophane Receptor for Bromide Ion Recognition in Aqueous Media

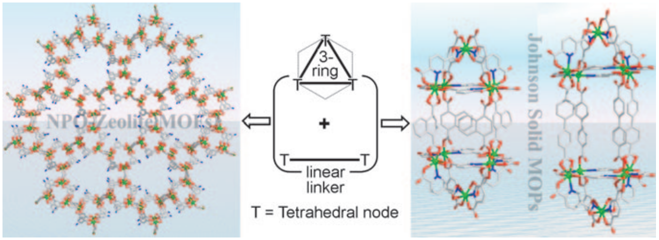


A bidentate halogen-bonding bromoimidazoliophane receptor selectively binds bromide ions in competitive aqueous media (see picture, gray = carbon, blue = nitrogen, brown = bromine). The bromide ions are bound by cooperative convergent bromine atom/halogen-bonding halide anion interactions.

Metal–Organic Composites

S.-T. Zheng, F. Zuo, T. Wu, B. Irfanoglu,
C. Chou, R. A. Nieto, P. Feng,
X. Bu* **1849 – 1852**

Cooperative Assembly of Three-Ring-Based Zeolite-Type Metal–Organic Frameworks and Johnson-Type Dodecahedra

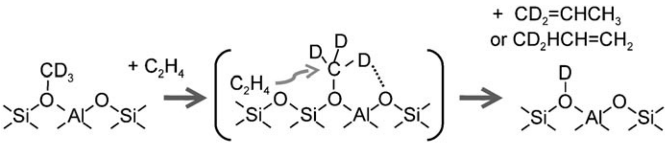


Two birds with one stone: Cooperative assembly of four-connected indium nodes with two symmetry-complementary ligands leads to both three-ring-based zeolite-type metal–organic frameworks (NPO-type) and the Johnson-type metal–organic polyhedra shown in the picture (gray C, green In, blue N, red O). The NPO-zeolite compounds behave as semiconductors and exhibit photocatalytic activity for the generation of dihydrogen from water under ultraviolet irradiation.

Methanol Activation

H. Yamazaki, H. Shima, H. Imai, T. Yokoi,
T. Tatsumi, J. N. Kondo* **1853 – 1856**

Evidence for a “Carbene-like” Intermediate during the Reaction of Methoxy Species with Light Alkenes on H-ZSM-5



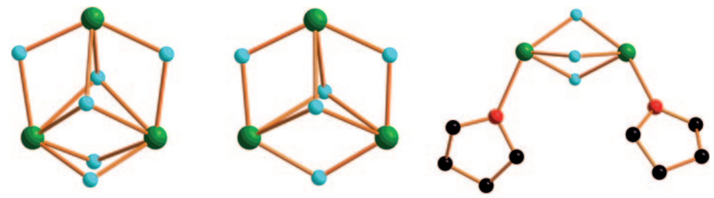
Secrets revealed: IR spectroscopy shows that the recovered acidic hydroxy groups after the reaction of [D_3]methoxy groups with light alkenes on zeolites are all deuterated (see scheme). The results indicate that the reaction occurs through methylene rather than methyl units.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Rare-Earth Polyhydrides

J. Cheng, T. Shima, Z. Hou* **1857 – 1860**

Rare-Earth Polyhydride Complexes Bearing Bis(phosphinophenyl)amido Pincer Ligands



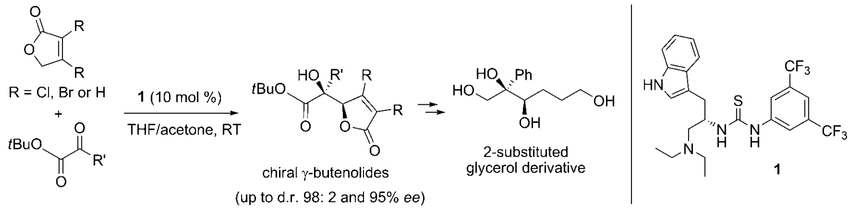
[{(Me-PNP^{iPr})LnH$_2$}$_3$] **A** [(Me-PNP^{iPr})$_3$Ln$_3$H$_5$][BPh$_4$] **B** [(Me-PNP^{iPr})$_2$Ln$_2$H$_3$(thf)$_2$][BPh$_4$] **C**

PNP downsizes hydride: Hydrogenolysis of dialkyl precursors results in trinuclear hexahydride complexes **A** (Me-PNP^{iPr} = {4-Me-2-(iPr$_2$P)-C$_6$H$_3$}$_2$N). Treatment with [NEt$_3$H][BPh$_4$] gives the first cationic trinuclear polyhydrides **B**. Cationic binuclear trihydride complexes **C** (only the central structural units are shown in the picture; C black, H blue, O red, Y green) have also been obtained for the first time.

Asymmetric Synthesis

J. Luo, H. Wang, X. Han, L.-W. Xu, J. Kwiatkowski, K.-W. Huang, Y. Lu* **1861 – 1864**

The Direct Asymmetric Vinylogous Aldol Reaction of Furanones with α-Ketoesters: Access to Chiral γ-Butenolides and Glycerol Derivatives

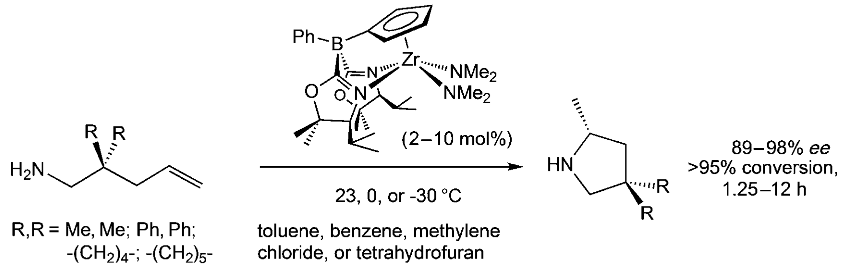


Twice as good: The title reaction using the tryptophan-derived bifunctional organic catalyst **1** has been developed. The reported method led to the synthesis of chiral γ-substituted butenolides in excellent yields, with high diastereo- and enantioselectivities. Facile synthesis of chiral glycerol derivatives containing a tertiary hydroxy group has also been demonstrated.

Asymmetric Hydroamination

K. Manna, S. Xu, A. D. Sadow* **1865 – 1868**

A Highly Enantioselective Zirconium Catalyst for Intramolecular Alkene Hydroamination: Significant Isotope Effects on Rate and Stereoselectivity



Zirconium catalysts sparkle: A new chiral zirconium complex has been used to catalyze hydroamination reactions to cyclize aminopentenes into 2-methylpyrrolidines (see scheme). The rate law supports a mechanism involving a reversible substrate–catalyst interaction that precedes the rate-determining step. A new mechanism for zirconium-catalyzed hydroamination has been proposed based on kinetic isotope effects and the significant effect of isotopic substitution on enantioselectivity.

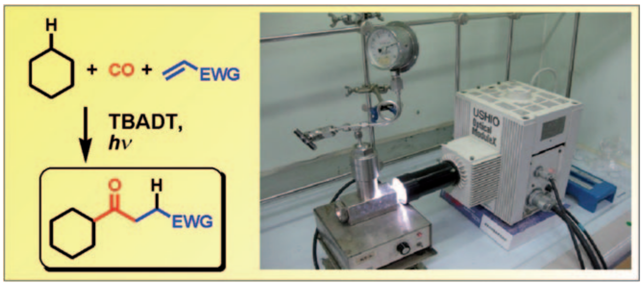
© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Contents

C–H Carbonylation

I. Ryu,* A. Tani, T. Fukuyama, D. Ravelli, M. Fagnoni,* A. Albini ______ **1869 – 1872**

Atom-Economical Synthesis of Unsymmetrical Ketones through Photocatalyzed C–H Activation of Alkanes and Coupling with CO and Electrophilic Alkenes

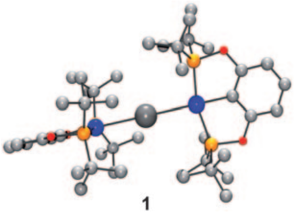


A three-component coupling between alkanes, CO, and electron-deficient alkenes in the presence of a catalytic amount of $(n\mathrm{Bu}_4\mathrm{N})_4\mathrm{W}_{10}\mathrm{O}_{32}$ (TBADT) has resulted in the efficient formation of unsymmetrical ketones. This process is based on the carbonylation of alkyl radicals photocatalytically generated by C–H activation of alkanes and the subsequent addition to alkenes (see scheme; EWG = electron-withdrawing group).

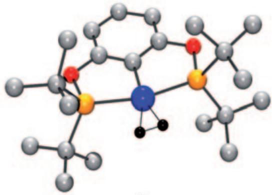
Cobalt Complexes

T. J. Hebden, A. J. St. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey* __________ **1873 – 1876**

Preparation of a Dihydrogen Complex of Cobalt



1



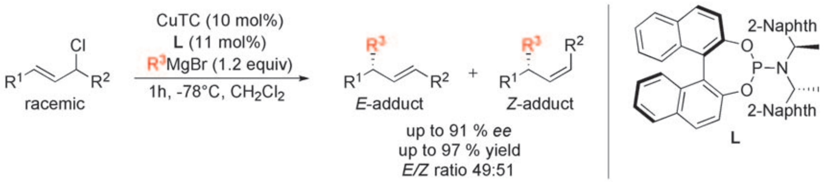
2

H_2 & Co.: A new pincer complex of $\mathrm{Co^{II}}$ has been synthesized. Reduction of this complex in the absence of additional ligands results in the formation of a highly reactive mercury-bridged dicobalt species (**1**). Subsequent introduction of H_2 at low temperature allows the observation of a rare dihydrogen complex of Co (**2**). Co blue, P yellow, O red, Hg dark gray.

Asymmetric Catalysis

J.-B. Langlois, A. Alexakis* _ **1877 – 1881**

Identification of a Valuable Kinetic Process in Copper-Catalyzed Asymmetric Allylic Alkylation



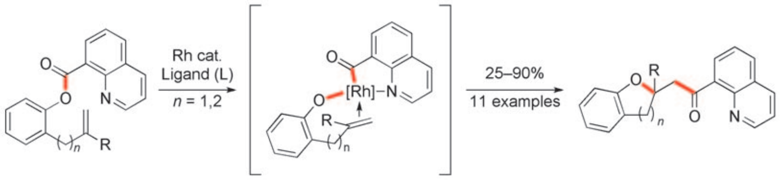
Copper bottomed: The application of a previously described process of dynamic kinetic asymmetric transformation to acyclic substrates allowed the identification of a relevant kinetic process in the title reaction (see scheme; CuTC = copper(I) thiophencarboxylate, Naphth = naphthyl). The optimization of the reaction conditions and generality of the method, as well as mechanistic considerations are disclosed.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

C−O Activation

G. T. Hoang, V. J. Reddy, H. H. K. Nguyen, C. J. Douglas* ———— **1882 – 1884**

Insertion of an Alkene into an Ester: Intramolecular Oxyacylation Reaction of Alkenes through Acyl C−O Bond Activation

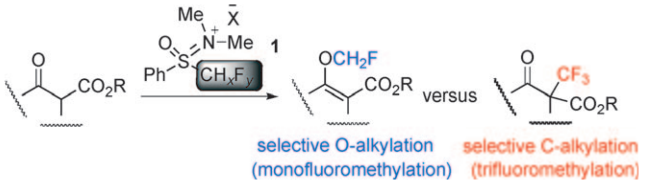


Atom economy and esters: compatible now! The first catalytic insertion of a C=C bond into an acyl C−O bond was achieved using rhodium catalysts (see scheme). The products are β-alkoxy ketones with a fully substituted carbon center. Quinoline chelating groups were employed to stabilize the Rh-alkoxide intermediate.

C−O Bond Formation

Y. Nomura, E. Tokunaga, N. Shibata* ———— **1885 – 1889**

Inherent Oxygen Preference in Enolate Monofluoromethylation and a Synthetic Entry to Monofluoromethyl Ethers

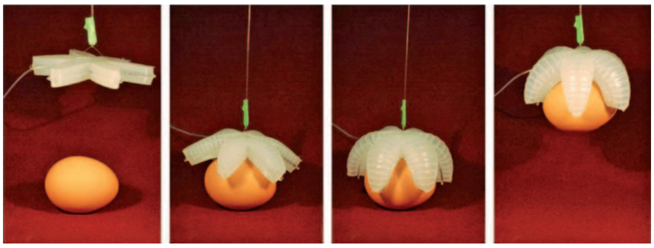


Expect the unexpected: The self-stable salts **1**, X = OTf, PF$_6$, $x = 2$, $y = 1$, developed for electrophilic monofluoromethylation showed inherent selectivity for the O-alkylation of enolates, thus providing access to monofluoromethyl ethers, which are difficult to obtain by the direct electrophilic fluoromethylation of alcohols. Salt **1**, X = BF$_4$, $x = 0$, $y = 3$, in contrast leads to C-alkylated products.

Chemical Robotics

F. Ilievski, A. D. Mazzeo, R. F. Shepherd, X. Chen, G. M. Whitesides* **1890 – 1895**

Soft Robotics for Chemists

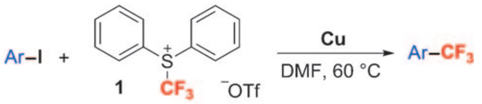


Soft robots: A methodology based on embedded pneumatic networks (PneuNets) is described that enables large-amplitude actuations in soft elastomers by pressurizing embedded channels. Examples include a structure that can change its curvature from convex to concave, and devices that act as compliant grippers for handling fragile objects (e.g., a chicken egg).

Synthetic Methods

C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao* ———— **1896 – 1900**

Copper-Mediated Trifluoromethylation of Heteroaromatic Compounds by Trifluoromethyl Sulfonium Salts

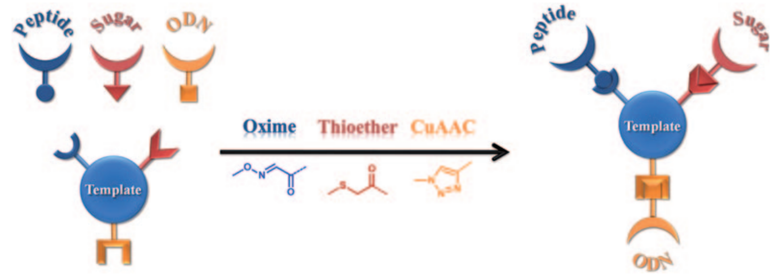


Copper is king! A convenient method for the synthesis of trifluoromethylated heteroaromatic compounds under mild conditions has been developed based on the observation that **1** can be reduced by certain metals (see scheme). Substrate **1** is assumed to be reduced by copper via a single-electron transfer mechanism, and CuCF$_3$ is the most probable intermediate in this reaction. DMF = *N*,*N*-dimethylformamide, Tf = triflate.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

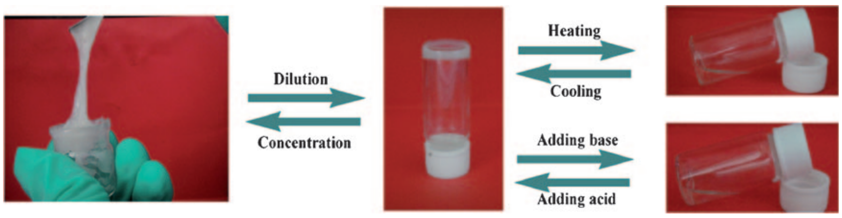
Contents

Biomolecular Synthesis



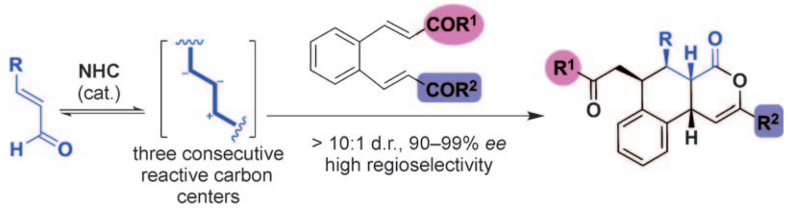
Three into one will go: The consecutive combination of three orthogonal chemoselective reactions (oxime ligation, thioether addition, and copper(I)-catalyzed alkyne–azide cycloaddition (CuAAC)) in a sequential one-pot approach allows the syntheses of highly sophisticated biomolecular compounds without intervening isolations and protection schemes (see picture; ODN = oligodeoxynucleotide).

Supramolecular Polymers



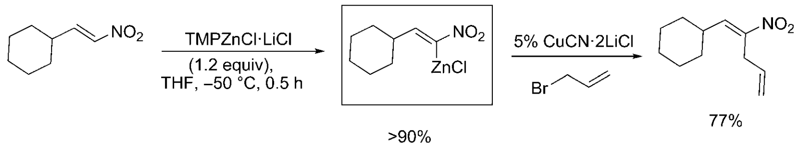
A host–guest recognition motif based on a crown ether moiety was employed to construct a supramolecular polymer gel from a low molecular weight A–B monomer. Reversible thermo- and pH-induced gel–sol transitions of the dual-responsive gel are demonstrated for the controlled release of rhodamine B.

Organocatalysis

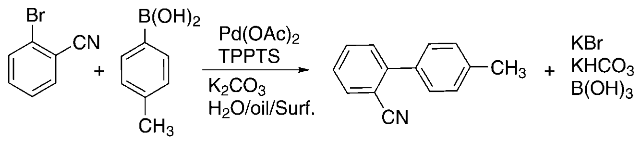


Three stereogenic centers in a row: The unconventional activation of enal compounds mediated by an N-heterocyclic carbene (NHC) has generated three consecutive reactive carbon centers that undergo highly regio- and stereoselective annulations with di(enone)s to generate benzotricyclic products containing multiple stereogenic centers (see scheme).

Metalation of Alkenes



Smooth and mild: Mg or Zn TMP bases (TMP = 2,2,6,6-tetramethylpiperidyl) allow the smooth metalation of various types of polyfunctional unsaturated substrates. Several sensitive functional groups such as ester, nitro, or trifluoromethylcarbonyl groups are tolerated. The new Zn or Mg intermediates undergo acylation, allylation, or cross-coupling reactions in satisfactory yields.

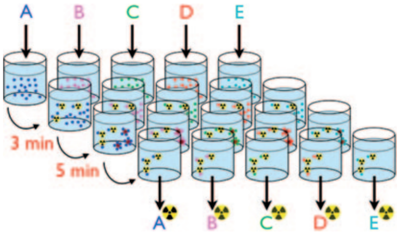


The reaction medium in the Suzuki coupling shown is a three-phase surfactant system. This medium offers advantages over conventional solvents in the reaction conversion and also in catalyst recovery. The reuse of the catalyst substantially increases the overall turnover number of the catalyst, a desirable factor in cost-effective industrial applications. TPPTS = 3,3′,3′′-phosphanetriyltris(benzenesulfonic acid) trisodium salt.

Catalyst Recycling

H. Nowothnick, J. Blum,
R. Schomäcker* ________ 1918 – 1921

Suzuki Coupling Reactions in Three-Phase Microemulsions



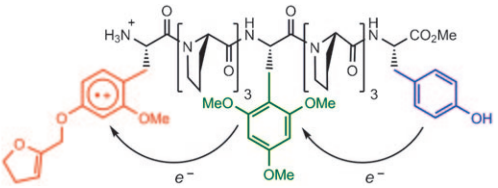
Pedal to the metal: The catalyst-free Diels–Alder cycloaddition of *trans*-cyclooctene and tetrazine was used to quickly and selectively generate an ^{18}F-labeled AZD2281 derivative from a tetrazine-linked precursor. The probe was tested in biological assays, and its targeted accumulation was confirmed in vivo. This protocol allows the parallel synthesis of a library of potential PET imaging agents in a short time, thus increasing the efficiency of lead compound development.

Targeted PET Imaging

T. Reiner, E. J. Keliher, S. Earley,
B. Marinelli, R. Weissleder* 1922 – 1925

Synthesis and In Vivo Imaging of a ^{18}F-Labeled PARP1 Inhibitor Using a Chemically Orthogonal Scavenger-Assisted High-Performance Method

---



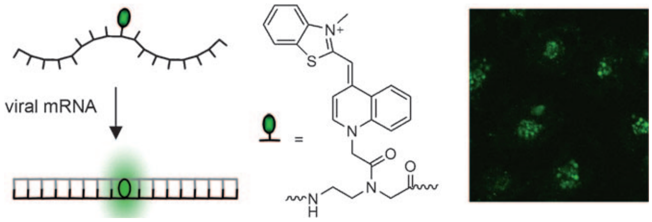
Charging off: The ammonium group in the peptide shown leads to a tenfold increase of the electron-transfer rate compared to that in a fully protected system. This is explained by Coulomb's law and the Marcus theory.

Electron Transfer

J. Gao, P. Müller, M. Wang, S. Eckhardt,
M. Lauz, K. M. Fromm,
B. Giese* ____________ 1926 – 1930

Electron Transfer in Peptides: The Influence of Charged Amino Acids

---



A message from the virus was detected by a peptide nucleic acid probe that contains thiazole orange as a fluorescent base surrogate (see picture). The high specificity and biostability of the probes lead to significant improvements to the signal-to-background ratio in imaging the mRNA from the influenza H1N1 virus in living infected cells.

Hybridization Probes

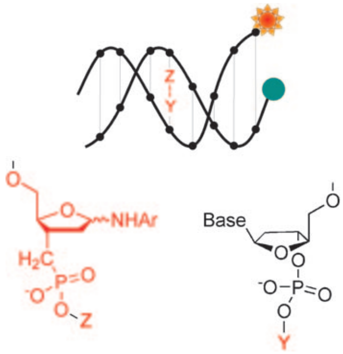
S. Kummer, A. Knoll, E. Socher, L. Bethge,
A. Herrmann,* O. Seitz* __ 1931 – 1934

Fluorescence Imaging of Influenza H1N1 mRNA in Living Infected Cells Using Single-Chromophore FIT-PNA

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Contents

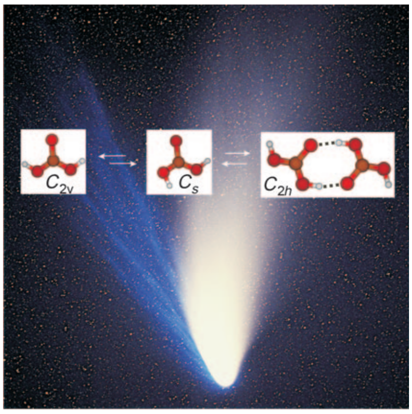
Base Pairing



Speed dating: A combinatorial assay was developed for screening a library of aromatic heterocyclic amines for their propensity to act as a complementary base Z in a DNA duplex. This assay may prove useful in speeding up the process of base-pair discovery for potential applications in biotechnology and synthetic biology.

IR Spectroscopy

Against all odds: Carbonic acid molecules were trapped from the gas phase in a solid noble-gas matrix at < 10 K and studied by IR spectroscopy. The ^{2}H and and ^{13}C isotopologues were also examined. Gas-phase carbonic acid is thought to exist as a 1:10:1 mixture of two monomeric conformers and the cyclic dimer $(H_2CO_3)_2$. This data is vital in the search for gas-phase carbonic acid in astrophysical environments.



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).

WILEY InterScience
DISCOVER SOMETHING GREAT

"**Hot Papers**" are chosen by the Editors for their importance in a rapidly evolving field of high current interest. A preview with the graphical abstracts of these articles can be found on the *Angewandte Chemie* homepage in Wiley InterScience at www.angewandte.org.

All articles in *Angewandte Chemie* are published online several weeks ahead of print. They are found under the "**EarlyView**" link on the journal's homepage in Wiley InterScience.

Service

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim