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:

*I. U. Khan, D. Zwanziger, I. Böhme, M. Javed, H. Naseer, S. W. Hyder, A. G. Beck-Sickinger**
Breast Cancer Diagnosis by Neuropeptide Y Analogues: From Synthesis to Clinical Application

K. Meindl, T. Schmiederer, K. Schneider, A. Reicke, D. Butz, S. Keller, H. Gühring, L. Vértesy, J. Wink, H. Hoffmann, M. Brönstrup, G. M. Sheldrick, R. D Süssmuth**
Labyrinthopeptins: A New Class of Carbacyclic Lantibiotics

*T. Mitsudome, K. Mizumoto, T. Mizugaki, K. Jitsukawa, K. Kaneda**
Wacker-Type Oxidation Using a $PdCl_2$–DMA Catalyst System under Copper-Free Conditions

*A. Pal, M. Bérubé, D. G. Hall**
Design, Synthesis, and Screening of a Library of Peptidyl Bisboroxoles as Low Molecular Weight Receptors for Complex Oligosaccharides in Water: Identification of a Receptor for the Tumor Marker TF-Antigen

Y.-Z. You, Z.-Q. Yu, M.-M. Cui, C.-Y. Hong**
Preparation of Photoluminescent Nanorings with Controllable Bioreducibility and Stimuli Responsiveness

*R. Kaminker, M. Lahav, L. Motiei, M. Vartanian, R. Popovitz-Biro, M. A. Iron, M. E. van der Boom**
Molecular Structure–Function Relations on the Optical Properties and Dimensions of Gold Nanoparticle Assemblies

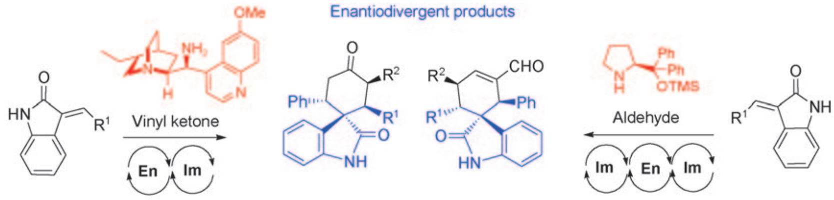
Author Profile

“In a nutshell, my research involves the development of innovative and powerful catalytic methods for the improvement of organic synthesis.
If I wasn’t a scientist, I would be unhappy …”
This and more about Frank Glorius can be found on page 842.

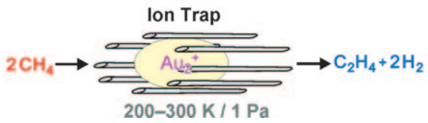
Books

Highlights

Organocatalysis

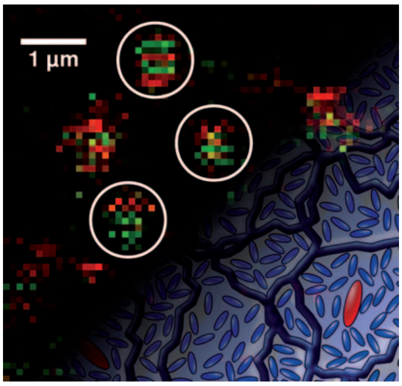


Synchronizing organocatalysis! By targeting structural and stereochemical complexity with organocascade reactions, distinct catalysts can form molecular frameworks in an enantiodivergent way. This goal was elegantly achieved for the asymmetric synthesis of quaternary carbon centers by two complementary routes employing cascades of either enamine or iminium catalysis (see scheme; En = enamine activation, Im = iminium activation).



Cold methane coupling: Recent experiments with trapped Au_2^+ clusters reveal a catalytic cycle for the dehydrogenative C–C coupling of methane to give ethene at temperatures between 200 and 300 K (see scheme). The key novelty of the work is the explicit exploration of the multicollisional regime, which represents an important step to bridge the pressure gap between model studies and real catalysis.

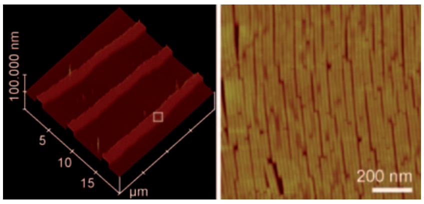
Reviews



Hit singles: Single-molecule optical approaches have opened a new way of exploring the properties of materials on nanometer scales. For example, a confocal image of perylenediimide, an organic dye molecule, in a thin film of supercooled glycerol reveals a spatially dynamical heterogeneity (see picture). This Review highlights the recent main uses of single molecules in studies of condensed matter, in particular soft and complex matter.

Communications

All lined up: Diverse patterns result from drying a solution of tobacco mosaic virus (TMV) particles in a glass capillary tube (see AFM images). The hierarchical assembled structure can be controlled by the particle concentration, the drying process, and the surface properties of the interior surface of the tube. The internally patterned tube can potentially be applied to directing the orientation of rat aortic smooth muscle cells.



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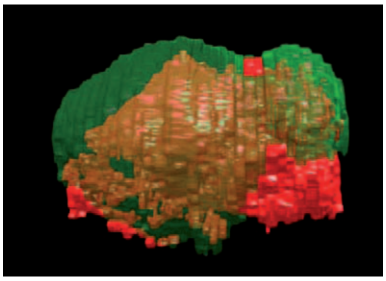
Imaging Mass Spectrometry

L. S. Eberlin, D. R. Ifa, C. Wu,
R. G. Cooks* ———— **873 – 876**

Three-Dimensional Vizualization of Mouse Brain by Lipid Analysis Using Ambient Ionization Mass Spectrometry

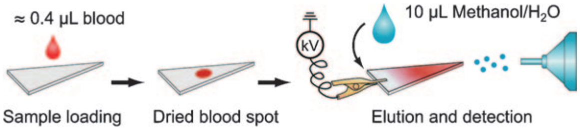


Imaging, not imagination: Three-dimensional (3D) images can be constructed from a set of 2D data acquired by desorption electrospray ionization (DESI) mass spectrometry. The 3D images show the spatial distributions of specific biomolecules in substructures of the mouse brain (see picture).

Mass Spectrometry

H. Wang, J. Liu, R. G. Cooks,*
Z. Ouyang* ———— **877 – 880**

Paper Spray for Direct Analysis of Complex Mixtures Using Mass Spectrometry

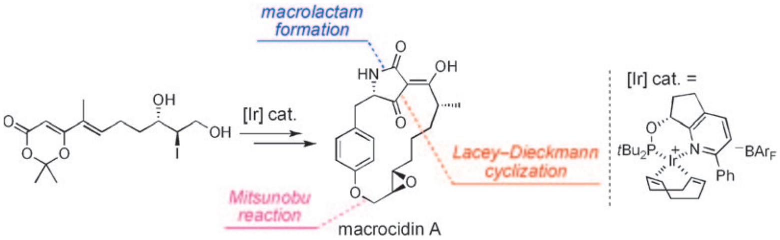


Complex mixtures can be ionized directly from paper for quantitative mass spectrometric analysis of trace components. Prior separations are an option.

Total Synthesis

T. Yoshinari, K. Ohmori, M. G. Schrems,
A. Pfaltz,* K. Suzuki* ———— **881 – 885**

Total Synthesis and Absolute Configuration of Macrocidin A, a Cyclophane Tetramic Acid Natural Product

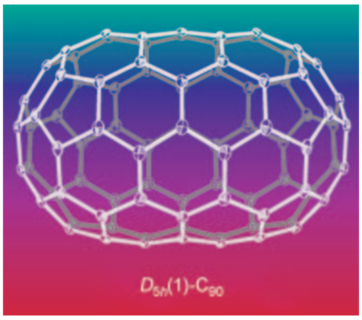


Stereocontrolled access to the cyclophane framework of macrocidin A has been achieved for the first time. The key steps include the iridium-catalyzed asymmetric hydrogenation without fission of the C–I bond, the macrolactam formation by intramolecular ketene trapping, and the Lacey–Dieckmann cyclization for the construction of the tetramic acid ring.

Fullerenes

H. Yang, C. M. Beavers, Z.-M. Wang,
A. Jiang, Z.-Y. Liu,* H.-X. Jin,*
B. Q. Mercado, M. M. Olmstead,*
A. L. Balch* ———— **886 – 890**

Isolation of a Small Carbon Nanotube: The Surprising Appearance of $D_{5h}(1)$-C_{90}



Totally tubular: The previously undetected higher fullerene $D_{5h}(1)$-C_{90} (see structure) was isolated as the major C_{90} isomer produced from Sm_2O_3-doped graphite rods and identified structurally by X-ray crystallography.

Frontiers of Chemistry:
From Molecules to Systems

A One-Day Symposium

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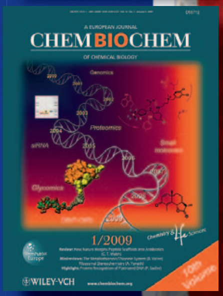
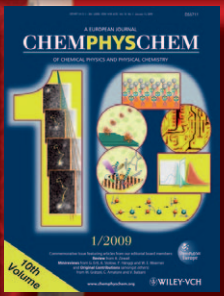
(near the Eiffel Tower and Les Invalides)

Celebrating 10 Years of





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


Marc Fontecave


Michael Grätzel


Michel Orrit


Nicolas Winssinger

Scientific committee

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

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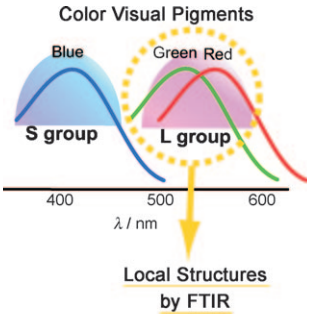
Color Vision

K. Katayama, Y. Furutani, H. Imai,*
H. Kandori* ________ 891 – 894

An FTIR Study of Monkey Green- and Red-Sensitive Visual Pigments

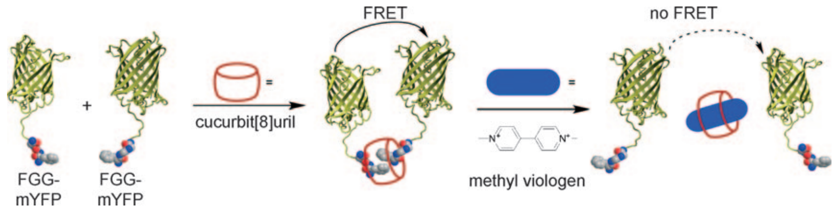
Seeing red (and green): The first structural insight into the color tuning of color visual pigments is obtained by light-induced FTIR studies of monkey green and red retinal pigments in D_2O. Their FTIR spectra are similar to those of rhodopsin in the low-frequency region but entirely different in the X–H and X–D stretching regions, providing insights into the chromophore–protein interactions in color pigments.



Protein Dimerization

H. D. Nguyen, D. T. Dang,
J. L. J. van Dongen,
L. Brunsveld* ________ 895 – 898

Protein Dimerization Induced by Supramolecular Interactions with Cucurbit[8]uril

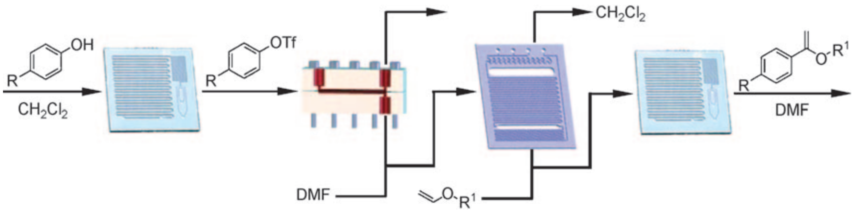


Hosted dimerization: Proteins such as yellow fluorescent protein (YFP) with an N-terminal FGG peptide motif form dimers mediated by supramolecular interactions with cucurbit[8]uril (see scheme). The protein dimerization, which is observed by FRET and size-exclusion chromatography, can be reversed with methyl viologen as a bioorthogonal ligand, which displaces the FGG motifs from the cucurbit[8]uril host.

Microreactor Networks

R. L. Hartman, J. R. Naber,
S. L. Buchwald,* K. F. Jensen* 899 – 903

Multistep Microchemical Synthesis Enabled by Microfluidic Distillation



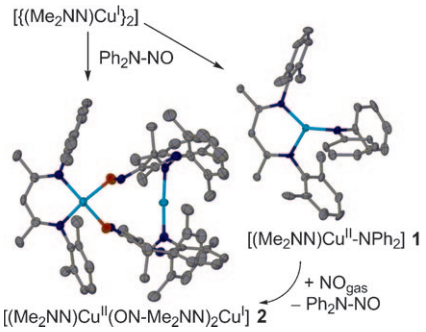
Microchemical solvent switch: A continuous-flow, multistep Heck synthesis was made possible by integrating microreactors, liquid–liquid extraction, and microfluidic distillation. The microfluidic distillation enabled solvent exchange from CH_2Cl_2 in the first reaction step to *N*,*N*-dimethylformamide (DMF) in the final reaction step.

Nitric Oxide

M. M. Melzer, S. Mossin, X. Dai,
A. M. Bartell, P. Kapoor, K. Meyer,
T. H. Warren* ________ 904 – 907

A Three-Coordinate Copper(II) Amide from Reductive Cleavage of a Nitrosamine

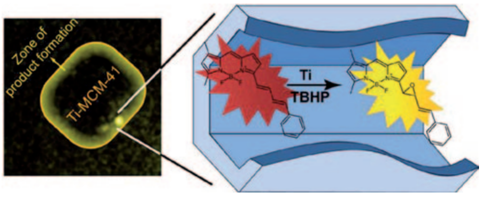
A NO-velty: A copper(I) β-diketiminate activates the nitrosamine Ph_2NNO to give a rare, three-coordinate copper(II) amide, $[(Me_2NN)Cu–NPh_2]$. Reaction of this amide with NO_{gas} returns Ph_2NNO as well as a mixed-valence species with NO-functionalized β-diketiminate ligands (see scheme; Cu light blue, N dark blue, O red). Thus, both the cleavage and formation of $R_2N–NO$ bonds may take place at a common copper center.



Heterogeneous Catalysis

G. De Cremer, M. B. J. Roeffaers,*
E. Bartholomeeusen, K. Lin, P. Dedecker,
P. P. Pescarmona, P. A. Jacobs,
D. E. De Vos, J. Hofkens,
B. F. Sels* ———— **908 – 911**

High-Resolution Single-Turnover Mapping Reveals Intraparticle Diffusion Limitation in Ti-MCM-41-Catalyzed Epoxidation

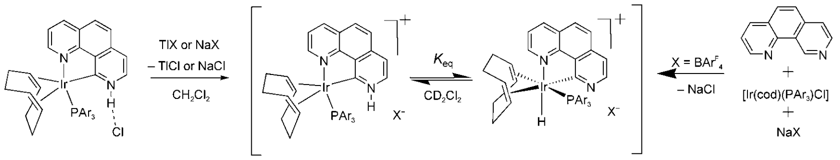


Shedding light on catalysis: For the first time, transport phenomena and their influence on catalysis are directly observed for individual catalytic particles by single-turnover mapping using high-resolution fluorescence microscopy. The Thiele modulus could be measured with just one experiment, proving the existence of diffusional limitations for the Ti-MCM-41 catalyzed epoxidation of a fluorescent reporter molecule (see picture; TBHP = *tert*-butylhydroperoxide).

N-Heterocyclic Carbenes

G. Song, Y. Su, R. A. Periana,
R. H. Crabtree, K. Han,* H. Zhang,*
X. Li* ———— **912 – 917**

Anion-Exchange-Triggered 1,3-Shift of an NH Proton to Iridium in Protic N-Heterocyclic Carbenes: Hydrogen-Bonding and Ion-Pairing Effects



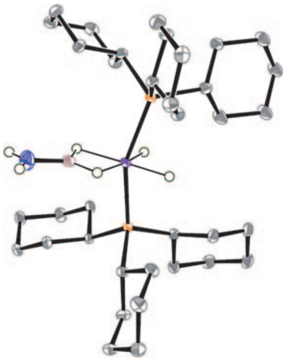
Proton release: A series of five-coordinate iridium(I) phosphine complexes with protic N-heterocyclic carbene ligands have been prepared which display N–H···Cl hydrogen bonding (see scheme; cod = 1,5-cyclooctadiene). Exchange of the chloride for less coordinating anions triggers the reversible 1,3-shift of the NH proton to the iridium, which is thought to proceed by a novel water-assisted proton-relay mechanism.

VIP

Reaction Intermediates

G. Alcaraz,* L. Vendier, E. Clot,
S. Sabo-Etienne* ———— **918 – 920**

Ruthenium Bis(σ-B–H) Aminoborane Complexes from Dehydrogenation of Amine–Boranes: Trapping of $H_2B{-}NH_2$



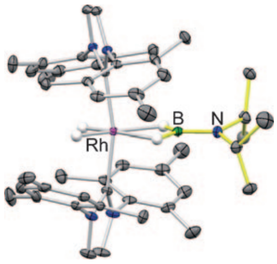
One small step for ammonia–borane: The simplest elementary aminoborane compound H_2BNH_2, which results from dehydrogenation of ammonia–borane, has been trapped by a ruthenium complex fragment leading to the isolation of a bis(σ-B–H) aminoborane complex. The analogous H_2BNHMe and H_2BNMe_2 complexes were also prepared. (Picture: ruthenium complex; Ru purple, P orange, N blue, B brown, H white.)

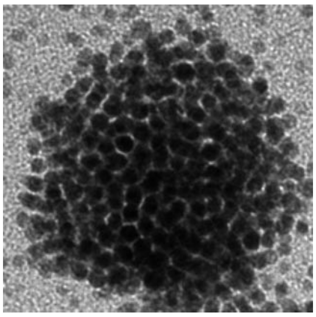
Aminoborane Complexes

C. Y. Tang, A. L. Thompson,
S. Aldridge* ———— **921 – 925**

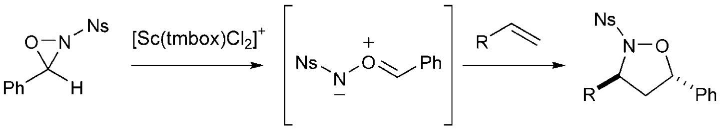
Rhodium and Iridium Aminoborane Complexes: Coordination Chemistry of BN Alkene Analogues

Side-on or end-on? Rhodium and iridium complexes featuring aminoboranes ($R_2N{=}BH_2$) as ligands have been synthesized and structurally characterized. Crystallographic measurements show that the ligands—in contrast to isoelectronic alkene donors—bind in an end-on fashion through a bis(σ-borane) binding motif (see structure).

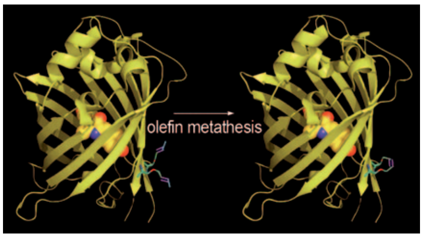




A new glue: Supramolecular assembly of gold nanoparticles (AuNPs, see picture) mediated by halogen bonding interactions is demonstrated. The primary time-dependent assembly of functionalized AuNPs controls the inner structure, whereas the appearance of the overall hybrid structures can be engineered by varying the concentration of the organic linker.

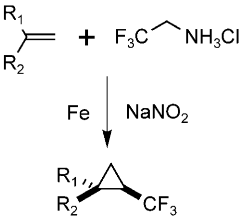


Dipoles apart: Unusual 1,3-dipolar carbonyl imines are generated in the presence of a bulky scandium(III) catalyst by undergoing a Lewis acid catalyzed rearrangement of *N*-sulfonyl oxaziridines. The 1,3-dipolar carbonyl imines then undergo subsequent cycloaddition with a variety of dipolarophiles. tmbox = 2,2′-isopropylidenebis(4,4-dimethyl-2-oxazoline).



Olefin-containing amino acids have been genetically introduced into proteins in *Saccharomyces cerevisiae* by orthogonal tRNA/aminoacyl-tRNA synthetase pairs. These nonnatural amino acids can be used for selective protein modification through olefin metathesis reactions.

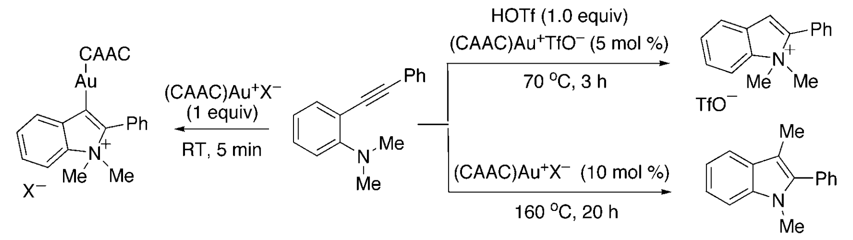
Let's avoid the risk! The title transformation has been developed for the synthesis of trifluoromethyl-substituted cyclopropane derivatives (see scheme). It avoids the preparation of trifluoromethyl diazomethane and merges a number of areas: water as a reaction medium, iron catalysis, and access to reactive intermediates under operationally safe conditions.



Gold Catalysis

X. Zeng, R. Kinjo, B. Donnadieu,
G. Bertrand* ———— **942 – 945**

Serendipitous Discovery of the Catalytic Hydroammoniumation and Methylamination of Alkynes



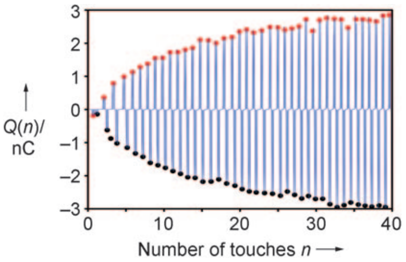
The gold rush: A cationic gold(I) complex, supported by a CAAC ligand, promotes the intramolecular addition of N—H or N—Me bonds (from ammonium salts or tertiary amines, respectively) to carbon–carbon triple bonds; the same complex allows for the isolation of vinylgold intermediates. X = $(C_6F_5)_4B$. CAAC = cyclic (alkyl)(amino)carbene.

Electrostatics

M. M. Apodaca, P. J. Wesson,
K. J. M. Bishop, M. A. Ratner,
B. A. Grzybowski* ———— **946 – 949**

Contact Electrification between Identical Materials

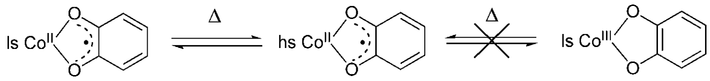
Ch-ch-ch-charges: Pieces of identical, atomically flat insulators separate a charge *Q* when brought into contact and then parted. Repeated contacts cause the magnitudes of the separated charges to increase monotonically (see picture). A theoretical model is presented that explains these phenomena by the inherent, molecular-scale fluctuations in the composition of the seemingly identical contacting surfaces.



Spin-Crossover Complexes

M. Graf, G. Wolmershäuser, H. Kelm,
S. Demeschko, F. Meyer,
H.-J. Krüger* ———— **950 – 953**

Temperature-Induced Spin-Transition in a Low-Spin Cobalt(II) Semiquinonate Complex

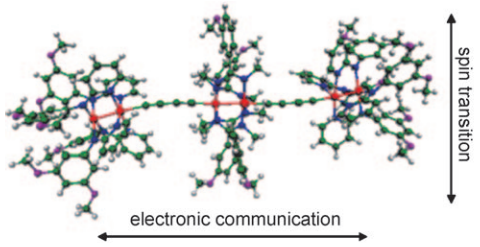


A new aspect of cobalt dioxolene chemistry: The preparation and characterization of the first low-spin cobalt(II) semiquinonate complex is described. The temperature-induced change of the spin state in this cobalt dioxolene complex (see scheme) is linked to a spin-crossover process rather than to valence tautomerism.

Organometallic Wires

J.-W. Ying, I. P.-C. Liu, B. Xi, Y. Song,
C. Campana, J.-L. Zuo, T. Ren* **954 – 957**

Linear Trimer of Diruthenium Linked by Butadiyn-Diyl Units:
A Unique Electronic Wire

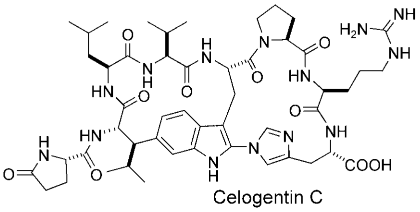


Ru communicating? Butadiyn-diyl bridges link three Ru_2 moieties together to give a molecular wire (see structure, red Ru, green C, blue N, purple O). Voltammetric, spectroscopic, and magnetic data all point to extensive electronic delocalization across the linear trimer.

C–H Activation

Y. Feng, G. Chen* ———— **958 – 961**

Total Synthesis of Celogentin C by Stereoselective C–H Activation



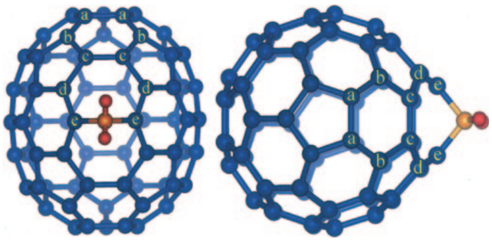
Celogentin C

A total gent: Inspired by the biosynthesis of celogentin C, a highly stereoselective and efficient palladium-catalyzed C–H functionalization strategy is employed to construct the key Leu-Trp linkage of this bicyclic compound. A streamlined synthesis is completed in 23 steps from simple amino acid building blocks.

Fullerenes

B. Li, C. Shu,* X. Lu,* L. Dunsch, Z. Chen, T. J. S. Dennis, Z. Shi, L. Jiang, T. Wang, W. Xu, C. Wang* ———— **962 – 966**

Addition of Carbene to the Equator of C_{70} To Produce the Most Stable $C_{71}H_2$ Isomer: 2aH-2(12)a-Homo(C_{70}-$D_{5h(6)}$)[5,6]-fullerene

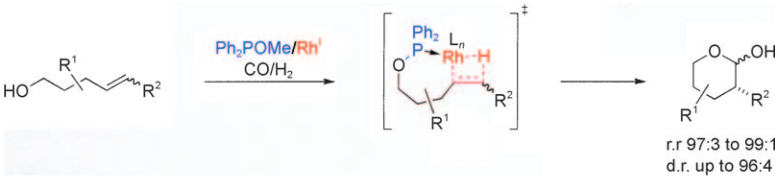


At long last, the elusive thermodynamically most stable isomer of $C_{71}H_2$ (see structure) has been synthesized through the addition of CH_2 across an equatorial bond of C_{70}: a site at which such a reaction is not kinetically favorable. Theoretical studies revealed that the pyrogenic synthetic method used enables reactants to overcome the higher activation barrier to equatorial addition.

Homogeneous Catalysis

C. U. Grünanger, B. Breit* ———— **967 – 970**

Remote Control of Regio- and Diastereoselectivity in the Hydroformylation of Bishomoallylic Alcohols with Catalytic Amounts of a Reversibly Bound Directing Group

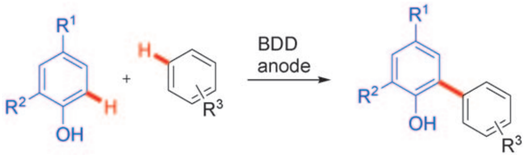


Remote and reversible! Phosphinites serve as reversibly bound directing groups for the remote control of the regio- and diastereoselective hydroformylation of bishomoallylic alcohols (see scheme; r.r: regioisomer ratio). The distance between the double bond and the functional hydroxy group to which the directing group is reversibly bound is the longest ever reported.

Biaryls

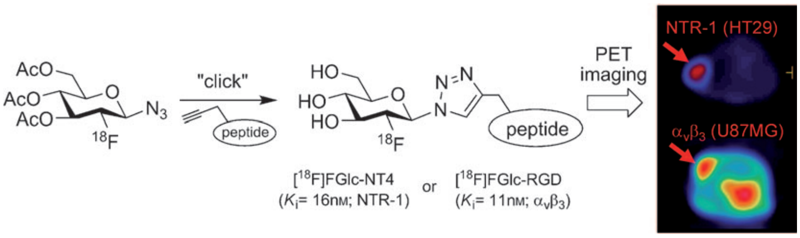
A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. R. Waldvogel* ———— **971 – 975**

Anodic Phenol–Arene Cross-Coupling Reaction on Boron-Doped Diamond Electrodes



Particularly sustainable: The anodic cross-coupling reaction between phenols and arenes can be performed on boron-doped diamond electrodes. The arylated products are formed directly and obtained, in some cases, with high selectivity. Since only hydrogen atoms are sacrificed in the course of reaction this methodology opens the door to a novel concept for biaryl formation.

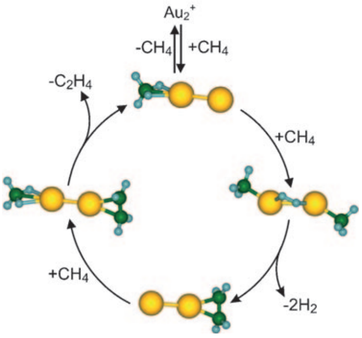
Molecular Imaging



Click for PET: An efficient strategy based on click chemistry has been developed for ^{18}F-labeling alkyne-bearing peptides with concomitant glycosylation. The mild conditions and general applicability of this reliable reaction gives access to a new class of ^{18}F-glycopeptide radiopharmaceuticals with improved biological properties for in vivo imaging studies by positron emission tomography (PET).

Methane Activation

Au pairs: Whereas one methane molecule is not dehydrogenated by free gold-dimer cations, the cooperative interaction of two methane ligands initiates a catalytic formation of ethylene. The cycle is closed by the adsorption of a third methane molecule that cooperatively activates the release of ethylene (see scheme yellow Au, green C, blue H). This cycle is derived from ab initio calculations and gas-phase reaction kinetics measurements.



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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