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:

Y. V. Geletii, B. Botar, P. Kögerler, D. A. Hillesheim, D. G. Musaev, C. L. Hill**
An All-Inorganic, Stable, and Highly Active Tetraruthenium Homogeneous Catalyst for Water Oxidation

*Z. Liu, A. Kumbhar, D. Xu, J. Zhang, Z. Sun, J. Fang**
Coreduction Colloidal Synthesis of III-V Nanocrystals: The Case of InP

*Y. H. Sehlleier, A. Verhoeven, M. Jansen**
Observation of Direct Bonds between Carbon and Nitrogen in Si–B–N–C Ceramic after Pyrolysis at 1400 °C

*E. Stavitski, M. H. F. Kox, I. Swart, F. M. de Groot, B. M. Weckhuysen**
In-Situ Synchrotron-Based IR Microspectroscopy To Study Catalytic Reactions in Zeolite Crystals

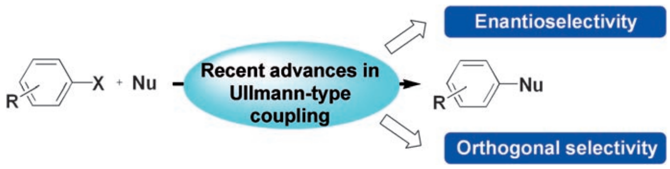
News

Books

Highlights

Better channeling: The insertion of amphiphilic, charged homo, graft, or block copolymers into lipid membranes is a way of forming defined membrane channels or pores. New insights into the mechanism of pore formation are discussed; for example, the picture shows the carpet mechanism for the insertion of amphiphilic graft polymers into a membrane.

Artifical Membrane Pores



Copper makes the difference: Important challenges have been overcome in copper-catalyzed Ullmann reactions since its renaissance in the early 2000s. Significant advances in this field have recently been made in regards to carrying out enantioselective and chemoselective arylation of nucleophiles (Nu) by using a copper catalyst (see scheme).

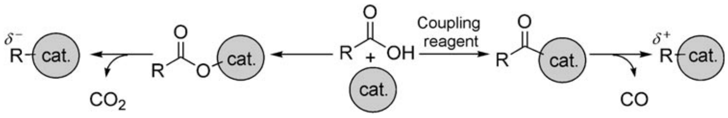
Arylation

Reviews

Carboxylic Acids

L. J. Gooßen,* N. Rodríguez,
K. Gooßen ______________ **3100–3120**

Carboxylic Acids as Substrates in Homogeneous Catalysis



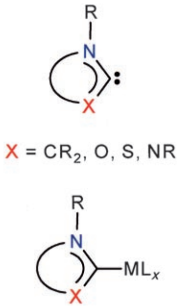
Ever increasing attention is being paid to transition-metal catalytic methods in which carboxylic acid derivatives act as substrates. Examples to be presented in this Review include the syntheses of esters, vinyl esters, biaryls, vinyl arenes, aldehydes, and ketones. The importance of these methods, especially in the context of sustainable synthetic chemistry, will be discussed.

Heterocyclic Carbenes

F. E. Hahn,* M. C. Jahnke __ **3122–3172**

Heterocyclic Carbenes: Synthesis and Coordination Chemistry

Carbene chameleons: Heterocyclic carbenes (see scheme) have gained great importance in synthetic organic and organometallic chemistry. The variation of the ring size and of the heteroatoms allows the properties of the carbenes and their metal complexes to be fine-tuned of over a wide range.

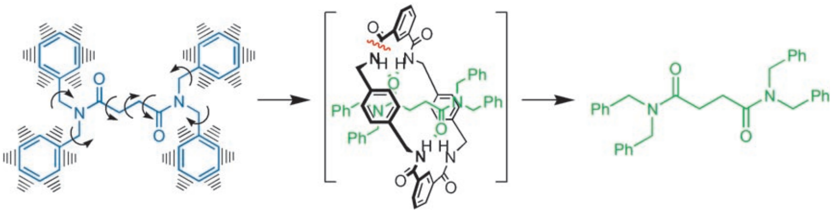


Communications

Conformational Control

A. M. Rijs, B. O. Crews, M. S. de Vries,*
J. S. Hannam, D. A. Leigh,* M. Fanti,
F. Zerbetto,* W. J. Buma* __ **3174–3179**

Shaping of a Conformationally Flexible Molecular Structure for Spectroscopy



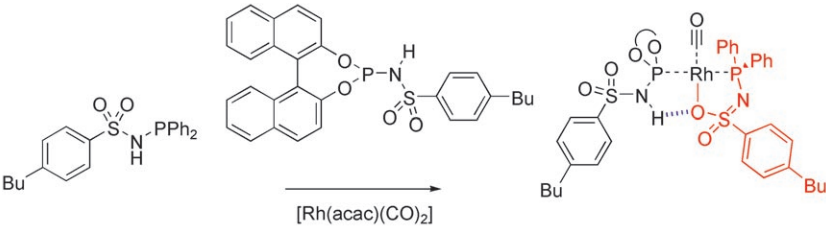
Chaperones for wild molecules: A molecule's conformational flexibility can be eliminated by enclosing it with a macrocyclic mold as a [2]rotaxane (see picture) that forces it into a specific shape. After rapid cooling, the mold is removed with a laser pulse. Through this process, the molded molecule becomes a suitable candidate for high-resolution electronic excitation spectroscopy.

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*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (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.

Supramolecular Ligands

F. W. Patureau, M. Kuil, A. J. Sandee,
J. N. H. Reek* ———— 3180 – 3183

METAMORPhos: Adaptive Supramolecular Ligands and Their Mechanistic Consequences for Asymmetric Hydrogenation

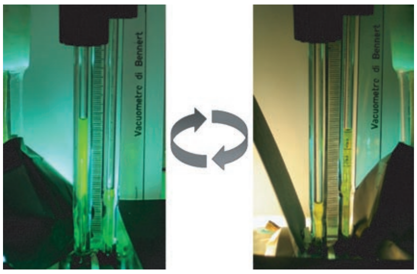


Adapt to react: METAMORPhos ligands are a class of flexible and adaptive hydrogen-bonded multidentate sulfonamide-based phosphorus ligands. Selective formation of complexes with two different METAMORPhos ligands (see scheme) that display unusual kinetic behavior leads to the proposal of a new mechanism. These complexes are highly reactive and enantioselective in the rhodium-catalyzed asymmetric hydrogenation of alkenes.

Energy Conversion

S. Masiero,* S. Lena, S. Pieraccini,
G. P. Spada ———— 3184 – 3187

The Direct Conversion of Light into Continuous Mechanical Energy by Photoreversible Self-Assembly: A Prototype of a Light-Powered Engine

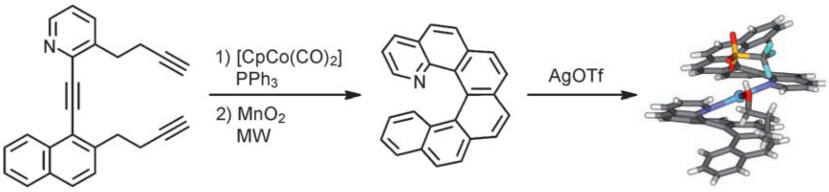


En route to a clean engine: The concentration of a chemical system containing an azobenzene derivative can be varied cyclically by light, and this variation has been exploited to produce continuous work. The cyclic concentration change of the system is the result of a light-controlled self-assembly/disassembly process.

Helical Structures

J. Míšek, F. Teplý, I. G. Stará,* M. Tichý,
D. Šaman, I. Císařová, P. Vojtíšek,
I. Starý* ———— 3188 – 3191

A Straightforward Route to Helically Chiral N-Heteroaromatic Compounds: Practical Synthesis of Racemic 1,14-Diaza[5]helicene and Optically Pure 1- and 2-Aza[6]helicenes

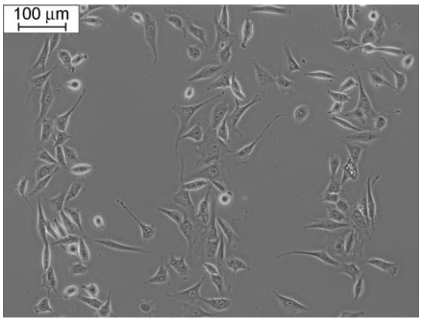


The taming of the screw: The Co^I-catalyzed cyclotrimerization of triynes and microwave (MW) assisted aromatization with MnO$_2$ are central to the practical synthesis of diaza[5]helicene and aza[6]helicenes. The aza[6]helicene racemates have been resolved, the absolute configuration of the enantiomers assigned, the energy barriers to racemization determined, and X-ray structures of their Ag complexes obtained (see picture; Cp = C_5H_5, OTf = triflate).

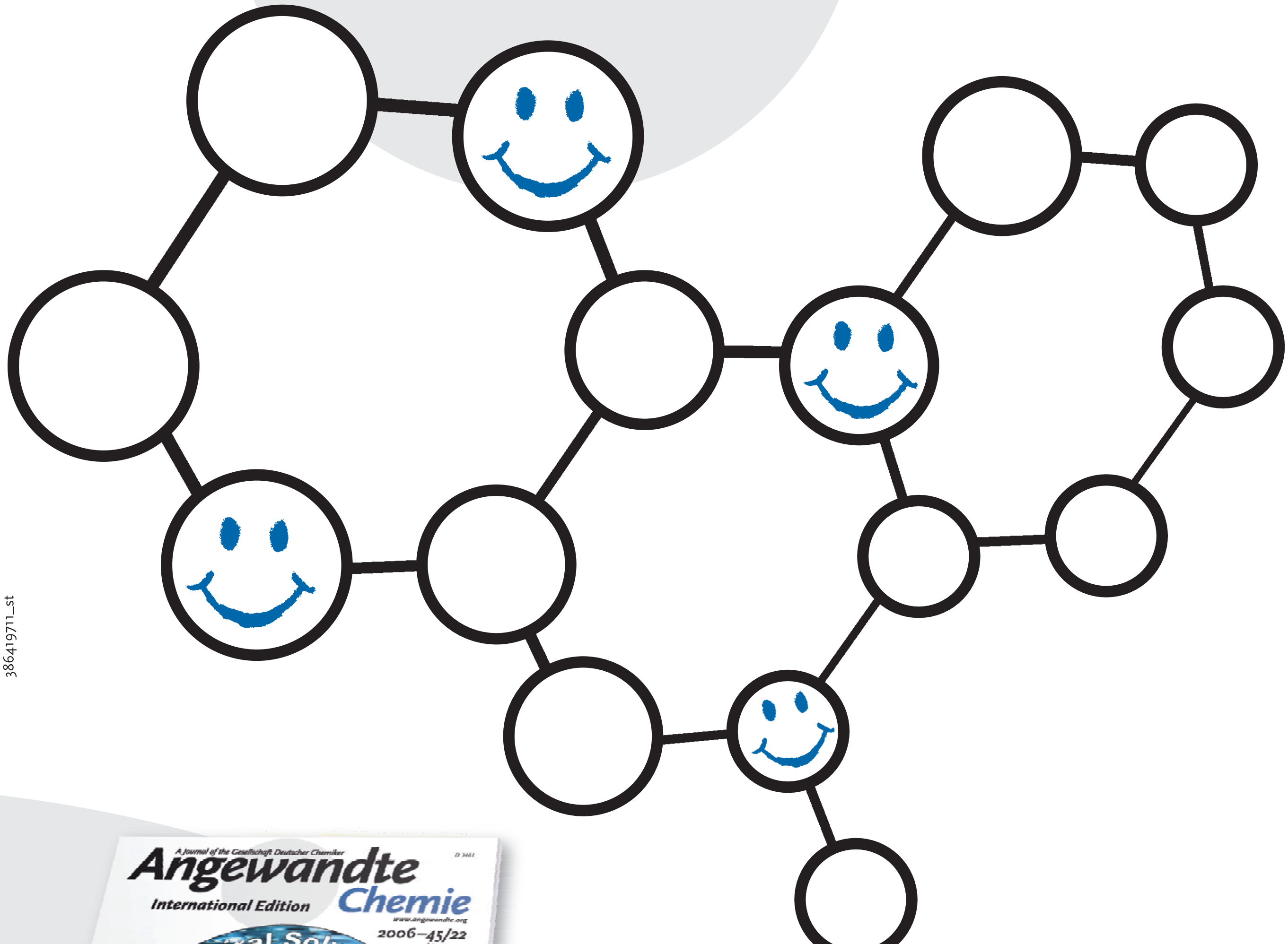
Cell–Surface Interactions

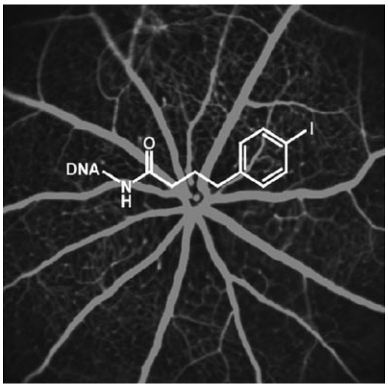
S. Petersen, J. M. Alonso, A. Specht,
P. Duodu, M. Goeldner,
A. del Campo* ———— 3192 – 3195

Phototriggering of Cell Adhesion by Caged Cyclic RGD Peptides



Restrained potential: A caged cyclic peptide attached to a surface is able to trigger cell attachment to the surface with spatiotemporal definition upon exposure to light ($\lambda = 351$ nm). The peptide shows no integrin-binding activity in its caged form, but mediates cell adhesion effectively after irradiation (see optical microscopy image of cells on a surface irradiated through a mask in bands 100 μm in width).





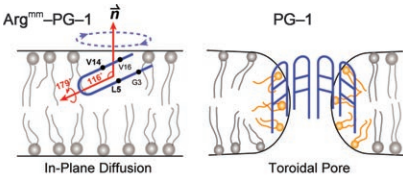
Seeing eye to eye: Plasma-protein binding is effective in improving the pharmacokinetic properties of otherwise short-lived molecules. One compound in a class of small portable albumin binders can be used to improve the in vivo circulatory half-life of two widely used contrast agents. It improves the imaging performance of fluorescein in angiographic analysis of the retina of mice (see picture).

Protein Binding

C. E. Dumelin, S. Trüssel, F. Buller, E. Trachsel, F. Bootz, Y. Zhang, L. Mannocci, S. C. Beck, M. Drumea-Mirancea, M. W. Seeliger, C. Baltes, T. Müggler, F. Kranz, M. Rudin, S. Melkko, J. Scheuermann, D. Neri* ______ **3196 – 3201**

A Portable Albumin Binder from a DNA-Encoded Chemical Library

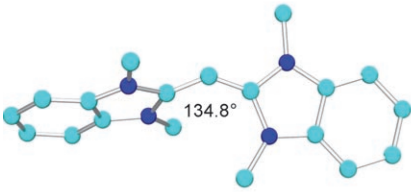
Barreling through: Guanidinium–phosphate hydrogen bonding significantly affects the structure and activity of the antimicrobial peptide PG-1. Solid-state NMR data show that a mutant of PG-1, having dimethylated Arg residues, adopts an in-plane orientation, interfacial location, and fast uniaxial motion around the membrane normal (see scheme). The less active mutant thus disrupts the membrane by in-plane diffusion, in contrast to the more active wild-type PG-1, which forms immobile transmembrane β-barrels to cause toroidal-pore membrane defects.



Transmembrane peptides

M. Tang, A. J. Waring, R. I. Lehrer, M. Hong* ______ **3202 – 3205**

Effects of Guanidinium–Phosphate Hydrogen Bonding on the Membrane-Bound Structure and Activity of an Arginine-Rich Membrane Peptide from Solid-State NMR Spectroscopy



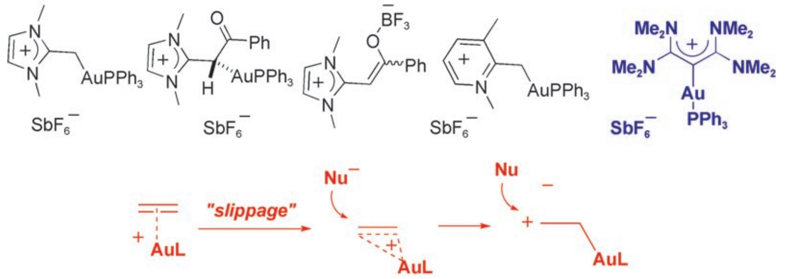
Pushed to the limit: Pushing $C{=}C$ π bonds to the breaking point by using a push–push substitution pattern forces allenes to bend (see structure; C light blue, N dark blue). An acyclic allene featuring a $C{=}C{=}C$ bond angle of 134.8° has been isolated in which the typically sp-hybridized central carbon atom approaches a configuration that has two lone pairs of electrons, and acts as a very strong η^1-donor ligand for transition metals.

Bent Allenes

C. A. Dyker, V. Lavallo, B. Donnadieu, G. Bertrand* ______ **3206 – 3209**

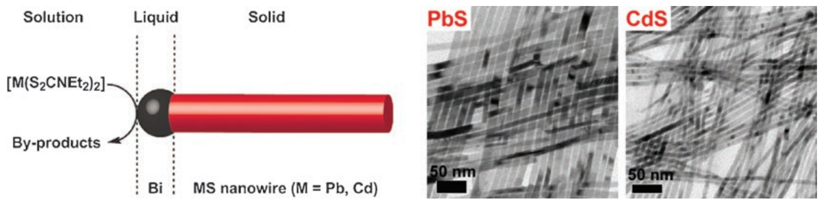
Synthesis of an Extremely Bent Acyclic Allene (A “Carbodicarbene”): A Strong Donor Ligand

Ligand Design



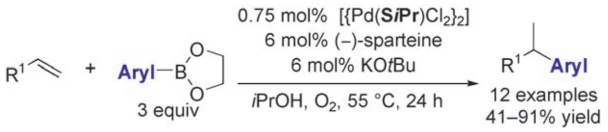
Carbophilic Lewis acids can polarize a coordinated π-bond by a slippage mechanism. A series of stable ylid- or enolate gold complexes of ene-1,1-diamines not only emulate this property, but also reveal the exceptional donor capacity of such electron-rich olefin ligands. Moreover, the first metal complex of a tetraaminoallene is reported, which features a prototype "carbodicarbene" ligand bound to a transition-metal template.

Nanowire Growth



All wired up! High-quality colloidal PbS and CdS nanowires were grown from Bi nanoparticles by the solution–liquid–solid (SLS) mechanism. The single-source-precursor strategy could provide a general approach for the synthesis of colloidal semiconductor nanowires.

Palladium Catalysis

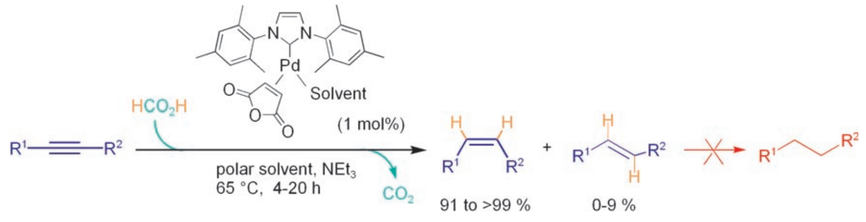


An oxidation exercise: An aerobic alcohol oxidation coupled with a regioselective palladium-catalyzed reductive functionalization of styrenes and arylboronic esters has been developed (see scheme). The mechanism is thought to proceed by initial oxidation of the solvent to generate a Pd^{II}-hydride species, which subsequently reacts with the alkene and arylboronic ester to ultimately generate a new C–C bond.

Transfer Hydrogenation

P. Hauwert, G. Maestri, J. W. Sprengers, M. Catellani, C. J. Elsevier* **3223 – 3226**

Transfer Semihydrogenation of Alkynes Catalyzed by a Zero-Valent Palladium N-Heterocyclic Carbene Complex

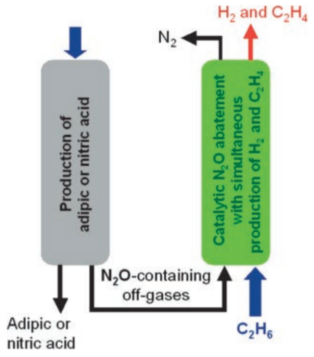


Beyond Lindlar and without hydrogen: Transfer hydrogenation of internal alkynes catalyzed by a palladium(0) catalyst containing an N-heterocyclic carbene ligand gives *Z* alkenes without over-reduction to alkanes (see scheme). Contrary to most transfer hydrogenations, ketones are not reduced. As such, this is the first catalyst that shows excellent stereo- and chemoselectivity for the semihydrogenation of alkynes without the need for hydrogen gas.

Environmental Chemistry

E. V. Kondratenko,* O. Ovsitser **3227 – 3229**

Catalytic Abatement of Nitrous Oxide Coupled with Selective Production of Hydrogen and Ethylene

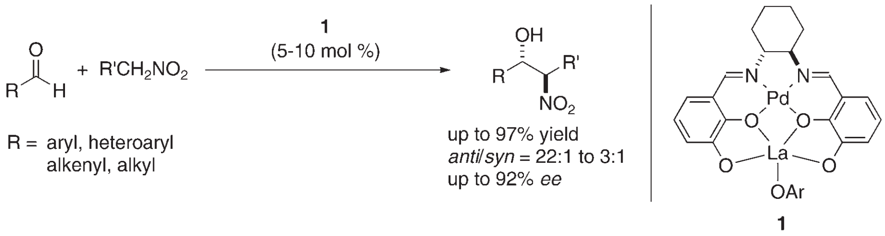


Chemicals come clean: Calcium oxide doped with small amounts of sodium oxide is used as catalyst in the abatement of N_2O by ethane to produce H_2 and ethylene. The ethylene yield and the H_2/C_2H_4 ratio are similar to those in the industrial steam cracking of ethane. The suggested process has potential for N_2O removal in the production of adipic and nitric acid (see picture).

Nitroaldol Reaction

S. Handa, K. Nagawa, Y. Sohtome, S. Matsunaga,* M. Shibasaki* **3230 – 3233**

A Heterobimetallic Pd/La/Schiff Base Complex for *anti*-Selective Catalytic Asymmetric Nitroaldol Reactions and Applications to Short Syntheses of β-Adrenoceptor Agonists

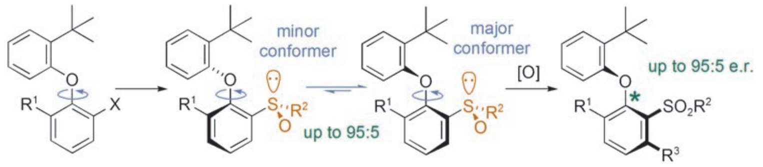


Two metals in a pod: The combination of Pd and La with a dinucleating Schiff base was developed for *anti* selectivity in the catalytic asymmetric nitroaldol reaction (see scheme). Short syntheses of β-adrenoceptor agonists by using the heterobimetallic catalyst are presented.

Atropisomeric Ethers

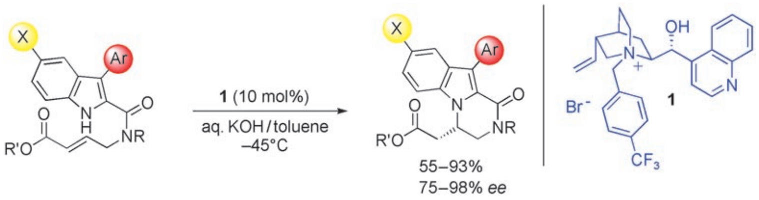
J. Clayden,* C. P. Worrall, W. J. Moran, M. Helliwell **3234 – 3237**

Enantioselective Synthesis of an Atropisomeric Diaryl Ether



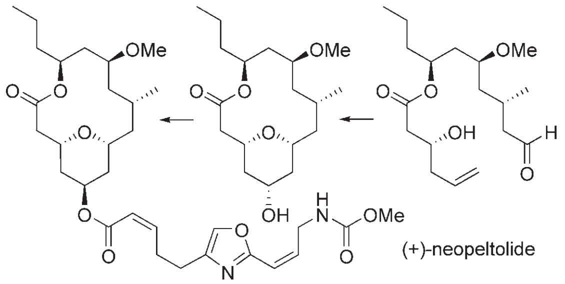
Twisted ethers: Introduction of a bulky alkylsulfinyl substituent *ortho* to the C–O axis of a diaryl ether imposes a powerful conformational preference (see scheme). The preference persists upon oxidation of the sulfoxide to a sulfone, leading to dynamic thermodynamic resolution of the atropisomeric ether. This is the first enantioselective synthesis of an atropisomeric diaryl ether not forming part of a macrocyclic ring.

Asymmetric Catalysis



Producing polycycles: A mild and direct stereocontrolled route to pharmacologically active pyrazino-indol-1-ones has been developed. The optimal phase-transfer conditions provide variously functionalized ring-closed compounds in high chemical and optical yields (see scheme; X = H, F, Cl, Me, OMe; Ar = Ph, β-naphthyl; R′ = *t*Bu, Et, Me; R = benzyl, *para*-methoxyphenyl).

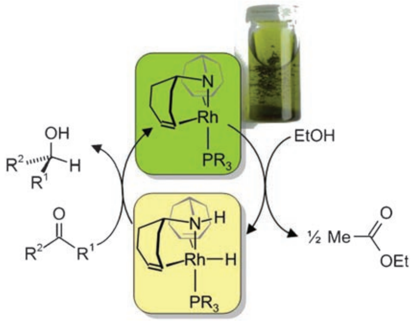
Natural Products



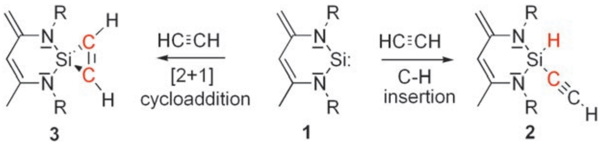
Rings within rings: The total synthesis of (+)-neopeltolide was accomplished by employing an intramolecular Prins macrocyclization of an aldehydic homoallylic alcohol intermediate (see scheme).

Homogeneous Catalysis

Catalysts take to the bottle: Rhodium amides with a saw-horse structure serve as very efficient catalysts for the transfer hydrogenation of ketones and activated olefins using ethanol as hydrogen donor. Under mild conditions, the corresponding alcohols and ethyl acetate are formed with high efficiency, with a turnover frequency above 500 000 h^{-1}.



N-Heterocyclic Silylenes

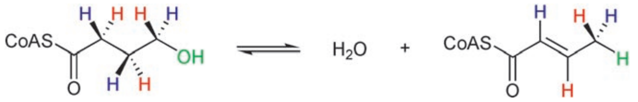


Jekyll and Hyde: Stable silylene **1** reacts readily with acetylene at room temperature to give 1,1-adduct **2**, whereas at −78 °C only silacycloprop-3-ene **3** is formed. Once **3** is present in the reaction mixture, it autocatalyzes its own generation even at room temperature. Both the facile silylene C–H bond insertion for terminal alkynes and the autocatalytic formation of silacycloprop-3-enes are unprecedented. R = 2,6-$iPr_2C_6H_3$.

Enzyme Mechanisms

P. Friedrich, D. J. Darley, B. T. Golding,
W. Buckel* ____________ 3254 – 3257

The Complete Stereochemistry of the Enzymatic Dehydration of 4-Hydroxybutyryl Coenzyme A to Crotonyl Coenzyme A



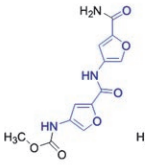
The stereospecific action of the microbial enzyme 4-hydroxybutyryl-CoA dehydratase on the three prochiral centers of its substrate 4-hydroxybutyryl-CoA can now be described as *anti* elimination of the 2*Re* and 3*Si* hydrogen atoms with retention of configuration during the substitution of the hydroxy group by a hydrogen atom. The results confirm the relationship of the dehydratase to acyl-CoA dehydrogenases and the view that the Fe_4S_4 cluster acts as a Lewis acid.

Marine Natural Products

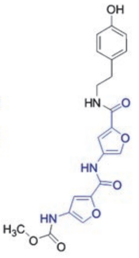
K. Schneider, S. Keller, F. E. Wolter, L. Röglin, W. Beil, O. Seitz, G. Nicholson, C. Bruntner, J. Riedlinger, H.-P. Fiedler,* R. D. Süssmuth* ________ 3258 – 3261

Proximicins A, B, and C—Antitumor Furan Analogues of Netropsin from the Marine Actinomycete *Verrucosispora* Induce Upregulation of p53 and the Cyclin Kinase Inhibitor p21

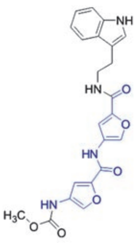
Drugs from the sea: Three new netropsin-type antibiotics (**1**–**3**) with a hitherto unknown furan core structure have been isolated from marine actinomycete strains and their structures elucidated by means of mass spectrometry and 2D NMR spectroscopy. The compounds show antitumor activity and, in contrast to netropsin, they induce upregulation of p53 and the cyclin kinase inhibitor p21.



1



2



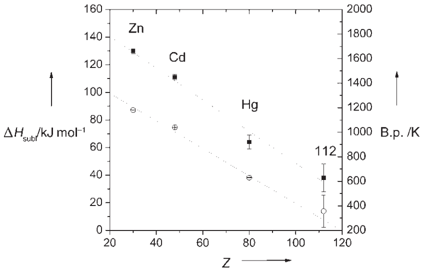
3

Transactinides

R. Eichler,* N. V. Aksenov, A. V. Belozerov, G. A. Bozhikov, V. I. Chepigin, S. N. Dmitriev, R. Dressler, H. W. Gäggeler, A. V. Gorshkov, M. G. Itkis, F. Haenssler, A. Laube, V. Y. Lebedev, O. N. Malyshev, Y. T. Oganessian, O. V. Petrushkin, D. Piguet, A. G. Popeko, P. Rasmussen, S. V. Shishkin, A. A. Serov, A. V. Shutov, A. I. Svirikhin, E. E. Tereshatov, G. K. Vostokin, M. Wegrzecki, A. V. Yeremin ____________ 3262 – 3266

Thermochemical and Physical Properties of Element 112

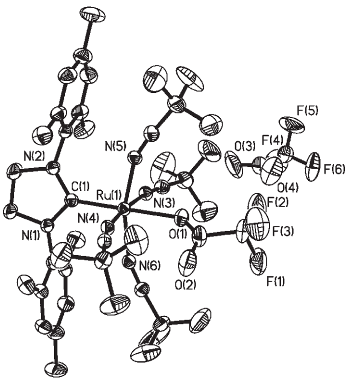
Every atom counts: New data for the adsorption chromatographic behavior of single atoms of element 112 confirm a metallic character involved in their interaction with a gold surface, similar to the lighter homologues Zn, Cd, and Hg. The elemental volatility of element 112 is much higher than that of lighter homologues of Group 12 of the periodic table, as empirically deduced from the experimental results.



Photochemical ROMP

D. Wang, K. Wurst, W. Knolle, U. Decker, L. Prager, S. Naumov, M. R. Buchmeiser* ________ 3267 – 3270

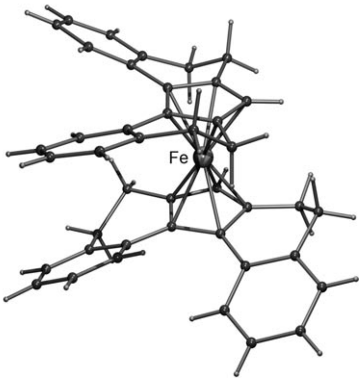
Cationic Ru^{II} Complexes with N-Heterocyclic Carbene Ligands for UV-Induced Ring-Opening Metathesis Polymerization



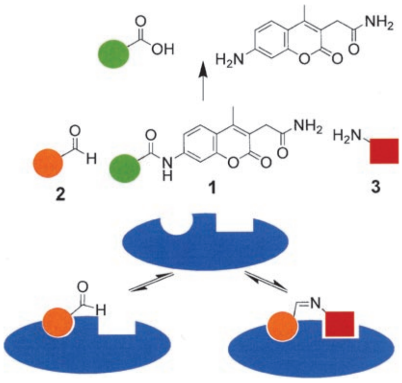
Open sesame: Novel cationic Ru^{II} complexes with N-heterocyclic carbene ligands (see structure) have been prepared and used as UV-triggerable photoinitiators for ring-opening metathesis polymerization. They may be used for the high-yield synthesis of bulk polymers as well as for surface functionalization. Laser pulse radiolysis and NMR spectroscopy experiments supported by quantum chemical calculations give insight into the initiation mechanism.

Metallocenes

Close relatives! The Pd-catalyzed hydrogenation of the "isolated" C=C double bonds of dibenzo[*c*,*g*]fluorenide coordinated to an Fe^{II} center confirms that the electronic structure of this ligand in organometallic compounds is related to that of cyclopentadienide. The resulting 3,4,3′,4′-tetrahydrodibenzo[*c*,*g*]fluorenide is a new chiral cyclopentadienide ligand (see picture for the molecular structure of the Fe complex).



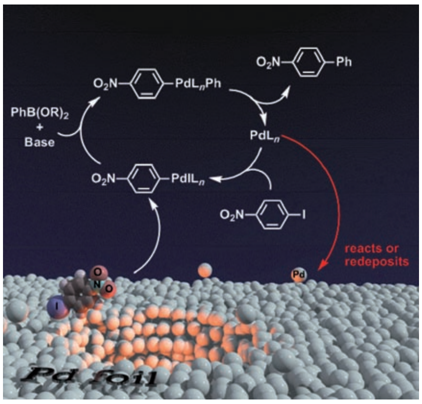
Medicinal Chemistry



A potential anti-SARS drug has been developed by dynamic ligation screening (DLS), by which nucleophilic fragments are directed to the protein's active site by reversible reaction with an aldehyde inhibitor. Their inhibitory effect is detected by competition with a fluorogenic enzyme substrate. With this concept, low-affinity fragments binding specifically to the active site are quickly identified in a functional enzyme assay.

Palladium Catalysis

Now you see it, now you don't: A specially designed reactor that heats only a small area of Pd foil during a Suzuki–Miyaura coupling permits observation of the surface changes during the reaction. Dissolution of Pd occurs only in the heated zone, and only in the presence of aryl iodide, whereas deposition of Pd occurs preferentially on the unheated zones adjacent to the reactive zone. SEM and XPS are employed to probe the surface before and after reaction.



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).

The issues for March 2008 appeared online on the following dates
Issue 10: February 15. · Issue 11: February 22. · Issue 12: March 3. · Issue 13: March 10

Service

Corrigendum

The last sentence in the left column on page 8802 of this Communication should read: “These two β-lactam-resistant bacterial cells contained different kinds of β-lactamases (TEM-1 in plasmid encoded *E. coli* Bl21 and ESBL; SHV-18 in *K. pneumoniae*).”
In the Supporting Information on page 1, the enzyme activity was not indicated correctly. The third sentence should read: “β-lactamases were obtained from Biologics Process Development, Inc, CA, USA and Sigma–Aldrich (6–18 units/mg corresponds to the amount of enzyme which hydrolyzes 1 μmol of benzylpenicillin per minute at pH 7.0 and 25 °C or 50–150 units/mg protein by using cephaloridine).”

A Simple and Specific Assay for Real-Time Colorimetric Visualization of β-Lactamase Activity by Using Gold Nanoparticles

R. Liu, R. Liew, J. Zhou,
B. Xing* **8799–8803**

Angew. Chem. Int. Ed. **2007**, *46*

DOI 10.1002/anie.200702773