VIP 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:

*A. Elahi, T. Fowowe, D. J. Caruana**
Dynamic Electrochemistry in Flame Plasma Electrolyte

J. Graton, Z. Wang, A.-M. Brossard, D. G. Monteiro, J.-Y. Questel, B. Linclau**
An Unexpected and Significantly Lower Hydrogen-Bond-Donating Capacity of Fluorohydrins Compared to Nonfluorinated Alcohols

*M. Kessler, S. Schüler, D. Hollmann, M. Klahn, T. Beweries, A. Spannenberg, A. Brückner, U. Rosenthal**
Photoassisted Ti–O Activation in a Decamethyltitanocene Dihydroxido Complex: Insights into the Elemental Steps of Water Splitting

*T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani, I. Krossing**
$[P_9]^+[Al(OR^F)_4]^-$, the Salt of a Homopolyatomic Phosphorus Cation

*J. Quinton, S. Kolodych, M. Chaumonet, V. Bevilacqua, M.-C. Nevers, H. Volland, S. Gabillet, P. Thuéry, C. Créminon, F. Taran**
Reaction Discovery by Using a Sandwich Immunoassay

R. Liu, G. Yuan, C. L. Joe, T. E. Lightburn, K. L. Tan, D. Wang**
Silicon Nanowires as Photoelectrodes for Carbon Dioxide Fixation

*L. M. H. Lai, I. Y. Goon, K. Chuah, M. Lim, F. Braet, R. Amal, J. J. Gooding**
The Biochemiresistor: An Ultrasensitive Biosensor for Small Organic Molecules

*W. Chaladaj, M. Corbet, A. Fürstner**
Total Synthesis of Neurymenolide A Based on a New Gold-Catalyzed Synthesis of 4-Hydroxy-2-pyrones

Author Profile

“If I were not a scientist, I would be an artist. My favorite band is Coldplay. …”
This and more about Bert Weckhuysen can be found on page 5790–5791.

News

B. M. Weckhuysen

M. Beller

F. Diederich

L. Cederbaum

Books

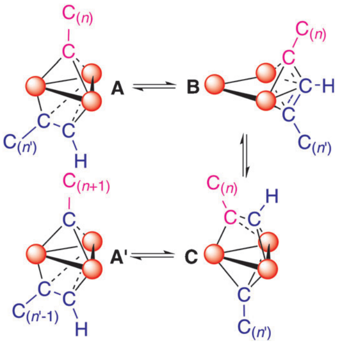
Highlights

Cluster Compounds

G. Lavigne* ______________ **5794 – 5796**

The Subtle Art of Bimetallic Activation: Juggling Carbenes, Hydrocarbons, and Hydride Ligands Between Metals

The selective redistribution of hydrocarbon chains $C_{(n)}$ on a polyhydrido triruthenium cyclopentadienyl complex (see scheme; Ru red spheres) involves a repeated sequence of face-to-face C–H group transfers (**A** to **C**) through the open cluster **B**, followed by individual concerted skeletal rearrangements on the two faces (**C** to **A′**). This process is just one of several spectacular examples illustrating the power of a molecular polymetallic system.



Essays

Lithium-Ion Battery

A. Yoshino* ______________ **5798 – 5800**

The Birth of the Lithium-Ion Battery

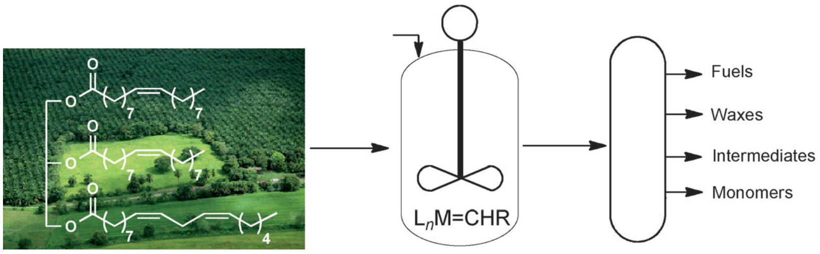
The moment of truth: The lithium-ion battery is currently the predominant power source for mobile phones, laptop computers, and many other portable electronic devices, and is being used increasingly in electric vehicles. Its inventor, A. Yoshino, describes the process by which the lithium-ion battery was first developed (picture shows the first test-tube cell) and made commercially practical. Successful safety tests marked the turning point in this work.

Minireviews

Renewable Resources

S. Chikkali, S. Mecking* ____ **5802 – 5808**

Refining of Plant Oils to Chemicals by Olefin Metathesis



The range of applications for plant oils in the chemical industry could be expanded by modern catalytic processes. The industrial application of olefin metathesis requires high catalyst activities, which influences the choice of the reaction. The mixture of fatty acids in a technical-grade plant oil substrate gives rise to a range of products. This determines the possible process schemes. Potentially novel chemicals and intermediates can be formed.

For the USA and Canada:
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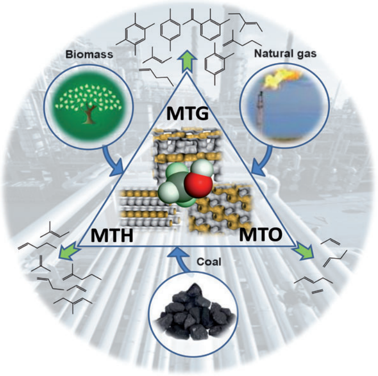
Reviews

Heterogeneous Catalysis



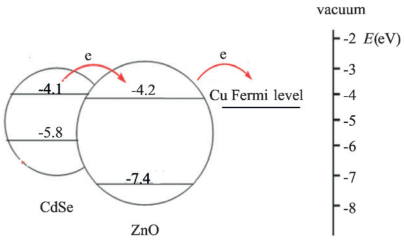
The active site of the methanol-to-hydrocarbons reaction has been identified as a hybrid site consisting of an organic molecule in close interaction with a Brønsted acidic proton on the zeolite lattice. With increasing internal volume, the organic intermediates change from alkenes via a mixture of alkenes and arenes to mainly arenes. Product selectivity reflects the site composition.

Communications

Heterogeneous Catalysts

VIP

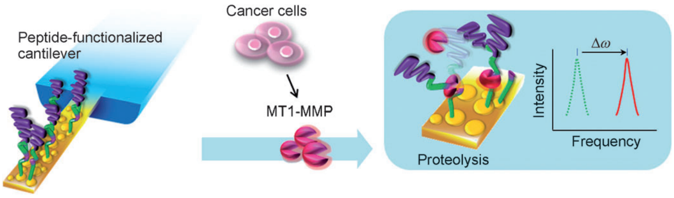
Frontispiece



Methanol from CO$_2$: For the hydrogenation of carbon dioxide, a marked increase in the methanol selectivity was observed when the reaction was catalyzed by Cu/rod-shaped ZnO/CdSe with heterojunction structure. Diffusion reflectance, photoluminescence, and ESR spectroscopies clearly indicated an increase in the electron density because of the incorporation of CdSe in the core–shell morphology of Cu/rod-shaped ZnO (see picture).

Biosensors

Inside Back Cover



Good vibrations: A bioassay using a resonant peptide-functionalized microcantilever enables the quantitative characterization of the proteolytic activity of membrane type-1 matrix metalloproteinase (MT1-MMP). In this assay, shifts in the frequency of the cantilever after specific proteolytic cleavage of the target peptides by MT1-MMP are measured (see picture).

VIP

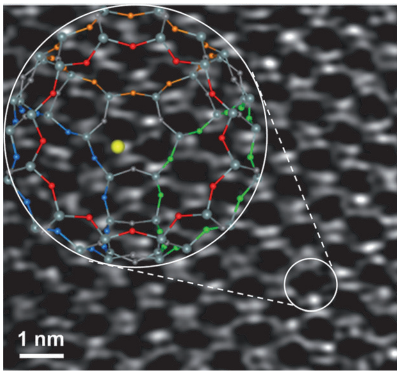
Gold Catalysis

J. Lu, C. Aydin, N. D. Browning,
B. C. Gates* ———— **5842 – 5846**

Imaging Isolated Gold Atom Catalytic Sites in Zeolite NaY

Back Cover

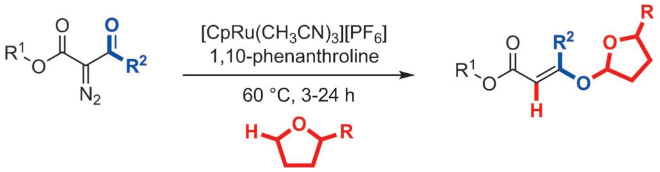
As good as atomic gold: Aberration-corrected scanning transmission electron microscopy images of zeolite NaY-supported mononuclear gold complexes, obtained with atomic resolution of the gold atoms, showed the locations of the gold complexes in the zeolite framework (see picture) and identified them as the catalytically active species for CO oxidation at 298 K and 1 bar.



C–O Coupling

C. Tortoreto, T. Achard, W. Zeghida,
M. Austeri, L. Guénée,
J. Lacour* ———— **5847 – 5851**

Enol Acetal Synthesis through Carbenoid C–H Insertion into Tetrahydrofuran Catalyzed by CpRu Complexes

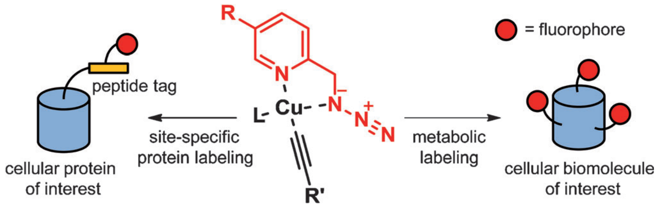


Intermolecular C–O instead of C–C bond formation is achieved with $[CpRu(CH_3CN)_3][PF_6]$ and diimine ligands as catalysts of the decomposition of α-diazo-β-ketoesters in THF leading to original products of 1,3 C–H insertion (see scheme).

Bioorthogonal Click Chemistry

C. Uttamapinant, A. Tangpeerachaikul,
S. Grecian, S. Clarke, U. Singh, P. Slade,
K. R. Gee, A. Y. Ting* ———— **5852 – 5856**

Fast, Cell-Compatible Click Chemistry with Copper-Chelating Azides for Biomolecular Labeling

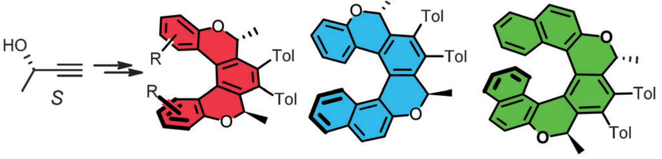


Bring your own copper: Copper-chelating azides undergo much faster click reactions (CuAAC) than nonchelating azides under a variety of biocompatible conditions. This kinetic enhancement allows site-specific protein labeling to be performed on the surface of living cells with only 10–40 µM Cu^I/Cu^{II} (see scheme). Detection sensitivity was also increased for CuAAC detection of alkyne-modified proteins and RNA.

Heterohelicenes

J. Žádný, A. Jančařík, A. Andronova,
M. Šámal, J. Vacek Chocholoušová,*
J. Vacek, R. Pohl, D. Šaman, I. Císařová,
I. G. Stará,* I. Starý* ———— **5857 – 5861**

A General Approach to Optically Pure [5]-, [6]-, and [7]Heterohelicenes



9 helicenes: all optically pure *M,R,R*

Spiral staircases: A general method for the preparation of optically pure [5]-, [6]-, and [7]heterohelicenes is based on a Co^I- or Ni^0-catalyzed diastereoselective [2+2+2] cycloisomerization of centrally chiral triynes to deliver helicenes comprising two 2*H*-pyran rings. The configuration, which can be predicted, does not depend on helicene length or functional groups present.

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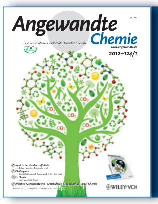

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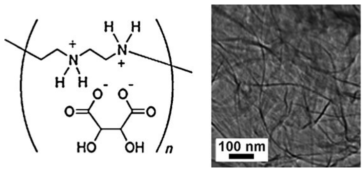
Chiral Silica

H. Matsukizono, R.-H. Jin* **5862 – 5865**

High-Temperature-Resistant Chiral Silica Generated on Chiral Crystalline Templates at Neutral pH and Ambient Conditions

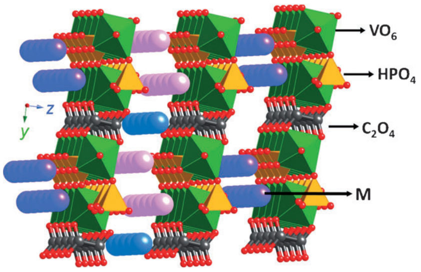


Crystalline and chiral supramolecular complexes can be self-assembled from linear polyethyleneimine and D- or L-tartaric acid. These complexes act as templates to direct nanofiber-based chiral silica, which showed remarkable chiroptical properties and remained chiral even after sintering at ultrahigh temperatures. Achiral molecules and gold nanoparticles bound to the chiral silica became active in CD spectra owing to induced chirality.

Hybrid Cathode Materials

M. Nagarathinam, K. Saravanan, E. J. H. Phua, M. V. Reddy,* B. V. R. Chowdari, J. J. Vittal* **5866 – 5870**

Redox-Active Metal-Centered Oxalato Phosphate Open Framework Cathode Materials for Lithium Ion Batteries

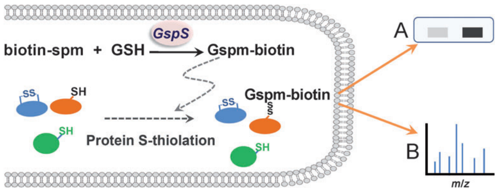


MOP(OF) up the lithium: Metal organic–phosphate open framework materials, for example $K_{2.5}[(VO)_2(HPO_4)_{1.5}(PO_4)_{0.5}(C_2O_4)]$ (see scheme), are investigated as hybrid cathode materials for lithium ion batteries. The redox-active metal center, robustness, available two-dimensional migration pathways in the *ab* plane, and cavities along the *c* axis for the migration of the alkali metal ions allow the rapid insertion and extraction of alkali metal ions.

Proteomics

B.-Y. Chiang, C.-C. Chou, F.-T. Hsieh, S. Gao, J. C.-Y. Lin, S.-H. Lin, T.-C. Chen, K.-H. Khoo,* C.-H. Lin* **5871 – 5875**

In Vivo Tagging and Characterization of S-Glutathionylated Proteins by a Chemoenzymatic Method

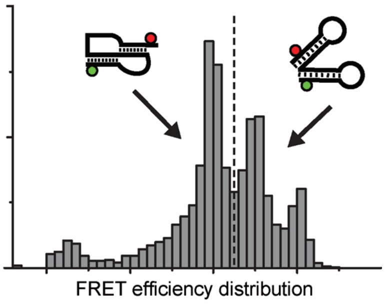


Glutathionylspermidine synthetase (GspS) was introduced into human cells to label endogenous glutathione (GSH) with biotinyl spermine (biotin-spm) for the identification of S-thiolated proteins. The proteins carrying Gspm-biotin can be detected by immunoblotting (A in figure). Enrichment by using the biotin tag enabled subsequent mass-spectrometry-based proteomic analysis (B) for site-specific identification of glutathionylated sites.

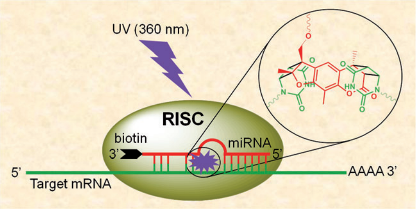
RNA Folding

M. Hengesbach, N.-K. Kim, J. Feigon, M. D. Stone* **5876 – 5879**

Single-Molecule FRET Reveals the Folding Dynamics of the Human Telomerase RNA Pseudoknot Domain

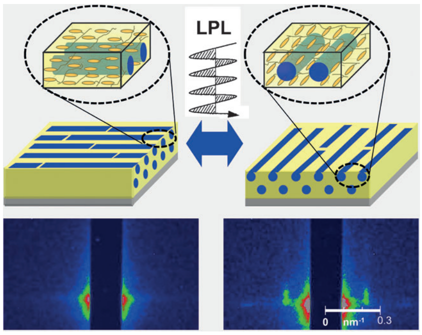


Do knot FRET: Single-molecule FRET was used to analyze the folding of human telomerase RNA (see scheme) and allowed discrimination between the correctly folded (left) and misfolded (right) structures. Analyzing the effects of various mutations showed that base pairing, triplex formation, and Mg^{2+} ion binding act synergistically in the folding of the pseudoknot structure in a functional hTR construct.



It's a TRAP! microRNAs (miRNAs) are noncoding small RNAs that consist of approximately 21 nucleotides and are assembled into an RNA-induced silencing complex (RISC), which suppresses target mRNA expression. An easy-to-use method called miRNA target RNA affinity purification (miR-TRAP) directly identifies miRNA targets in vivo. This method could be widely used to discover miRNA targets in various disease models under physiological conditions.

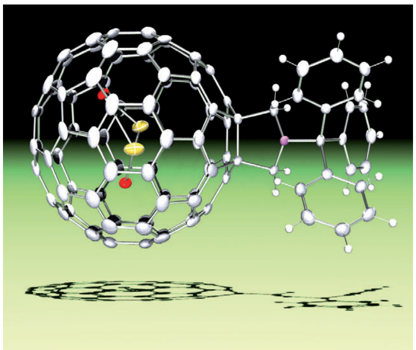
microRNA Target Identification



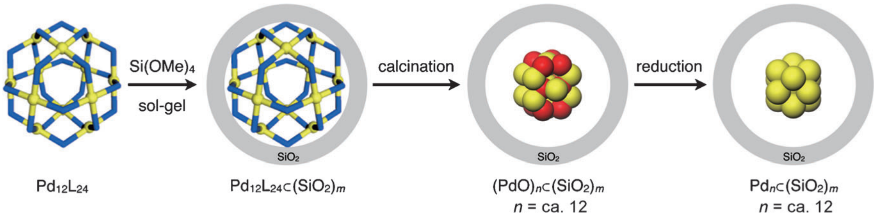
Light, (CCD) camera, action! Time-resolved synchrotron X-ray scattering measurements revealed that linear polarized light (LPL) caused reorientation of phase-separated mesoscopic amorphous cylinders within a light-responsive liquid crystalline (LC) matrix domain of a diblock copolymer (see scheme). Cooperative and synchronized motions occur at two hierarchical structures of the LC layer (molecular level) and the polymer domains (mesoscopic level).

Photoresponsive Polymers

It's a carbide! The long-believed $Sc_2@C_{2v}(17)\text{-}C_{84}$ is unambiguously identified as $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$. Its chemical properties were investigated by reaction with a 1,3-dipolar reagent. X-ray analyses of the major adduct (see image) reveal a [5,6]-closed structure. The addition pattern can be reasonably explained by frontier molecular orbital theory.



Carbide Fullerenes



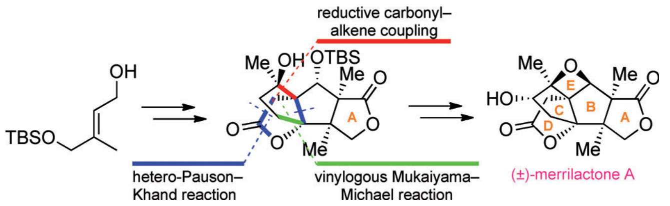
Imprisoned palladium: A unique approach is developed to incarcerate metal clusters with strictly controlled *n* values within hollow silica nanoparticles. A $Pd_{12}L_{24}$ spherical complex is used as a template for the hollow silica synthesis. The incarcerated $Pd_{12}L_{24}$ core is calcinated to give $(PdO)_n$ oxide clusters and subsequently reduced to Pd_n metal clusters within the protective hollow silica.

Metal Clusters

Natural Products Synthesis

J. Chen, P. Gao, F. Yu, Y. Yang, S. Zhu, H. Zhai* ________ 5897 – 5899

Total Synthesis of (±)-Merrilactone A

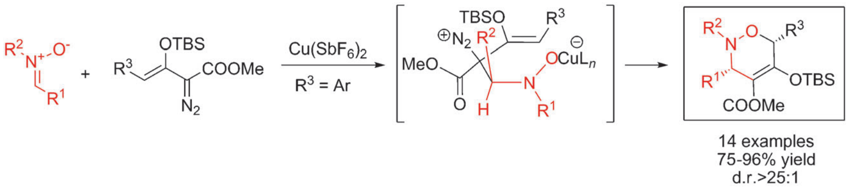


An efficient total synthesis of (±)-merrilactone A has been accomplished, featuring: 1) a Johnson–Claisen rearrangement and the subsequent deprotection–lactonization to generate the A ring, 2) an intramolecular hetero-Pauson–Khand reaction to construct the B and D rings, and 3) a vinylogous Mukaiyama–Michael reaction and reductive carbonyl–alkene coupling to assemble the C ring.

Synthetic Methods

Y. Qian, X. Xu, X. Wang, P. J. Zavalij, W. Hu, M. P. Doyle* ________ 5900 – 5903

Rhodium(II)- and Copper(II)-Catalyzed Reactions of Enol Diazoacetates with Nitrones: Metal Carbene versus Lewis Acid Directed Pathways

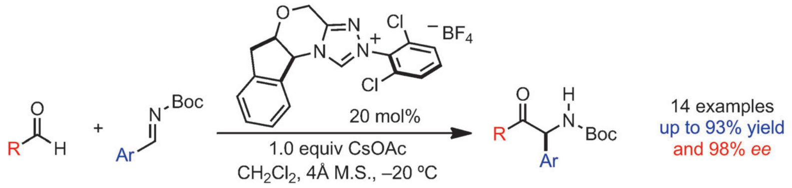


A complimentary cat.: Copper(II) hexafluoroantimonate catalyzes the formal [3+3] cycloaddition of Lewis acid activated nitrones and vinyl diazoacetates to produce 3,6-dihydro-1,2-oxazines in yields of up to 96% and diastereoselectivities greater than 25:1 (see scheme). This process compliments the metal carbene pathway that is catalyzed by rhodium(II) species.

Synthetic Methods

D. A. DiRocco, T. Rovis* ________ 5904 – 5906

Catalytic Asymmetric Cross-Aza-Benzoin Reactions of Aliphatic Aldehydes with N-Boc-Protected Imines

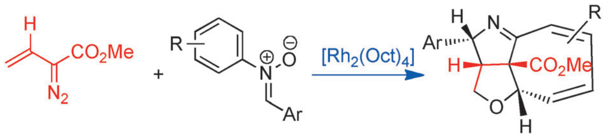


Crossed: A catalyst system has been developed that allows the direct asymmetric coupling of aliphatic aldehydes and N-Boc-protected imines in a cross-aza-benzoin reaction (see scheme; Boc = *tert*-butoxycarbonyl). The active catalyst is shown to react rapidly with the imine, however, the presence of an acid as cocatalyst renders this process reversible and allows the regeneration of the catalyst.

Cascade Reactions

X. Wang, Q. M. Abrahams, P. Y. Zavalij, M. P. Doyle* ________ 5907 – 5910

Highly Regio- and Stereoselective Dirhodium Vinylcarbene Induced Nitrone Cycloaddition with Subsequent Cascade Carbenoid Aromatic Cycloaddition/N–O Cleavage and Rearrangement

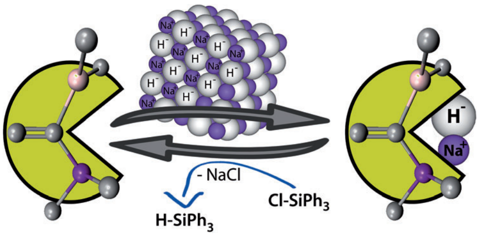


An abnormal cascade process provides a selective method for the preparation of tricyclic heterocycles. The cascade involves a metal carbene induced regioselective [3+2] cycloaddition, a Buchner reaction, and a [1,7]-oxygen migration, which occurs with N–O cleavage (see scheme). The products are formed with remarkable specificity.

Hydride Activation

C. Appelt, J. C. Slootweg,*
K. Lammertsma, W. Uhl* ___ **5911 – 5914**

A Phosphorus/Aluminum-Based Frustrated Lewis Pair as an Ion Pair Receptor: Alkali Metal Hydride Adducts and Phase-Transfer Catalysis

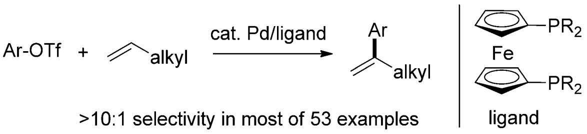


Helpful frustration: The geminal phosphorus/aluminum-based frustrated Lewis pair $(Mes_2P)(tBu_2Al)C{=}C(H)Ph$ (Mes = 2,4,6-$Me_3C_6H_2$) forms stable adducts with alkali metal hydrides (LiH, NaH, KH). These molecular hydride complexes display enhanced reactivity, which was demonstrated by the catalytic transformation of chlorotriphenylsilane to the corresponding hydride through a frontside S_N2-f@Si pathway.

Heck Reaction

L. Qin, X. Ren, Y. Lu, Y. Li,
J. Zhou* ___ **5915 – 5919**

Intermolecular Mizoroki–Heck Reaction of Aliphatic Olefins with High Selectivity for Substitution at the Internal Position

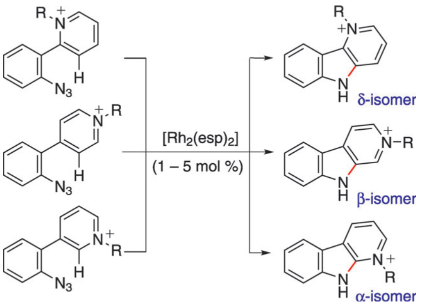


New ligand for old reaction: The title reaction of aryltriflates with aliphatic olefins leads to substitution at the internal position with high selectivity. The ratio of the desired isomer (shown in the scheme) to the sum of all other isomers is generally above 10:1. The key to success is the use of a ferrocene bisphosphine ligand (R = 1-naphthyl). The reaction can be easily scaled up, and minor isomers can be separated by chromatography.

Synthetic Methods

A. L. Pumphrey, H. Dong,
T. G. Driver* ___ **5920 – 5923**

Rh^{II}_2-Catalyzed Synthesis of α-, β-, or δ-Carbolines from Aryl Azides

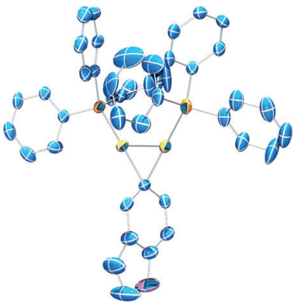


Approaching all isomers: A range of α-, β- and δ-carbolinium ions are readily available from *ortho*-substituted aryl azides using a rhodium(II) carboxylate catalyst (see scheme). The carbolinium ions are readily reduced to afford tryptolines or deprotonated to access pyridoindoles. This $[Rh^{II}_2]$-catalyzed C–H bond amination was used in the synthesis of (±)-horsfiline and neocryptolepine. esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionate.

Gold Aryl Complexes

J. E. Heckler, M. Zeller, A. D. Hunter,
T. G. Gray* ___ **5924 – 5928**

Geminally Diaurated Gold(I) Aryls from Boronic Acids

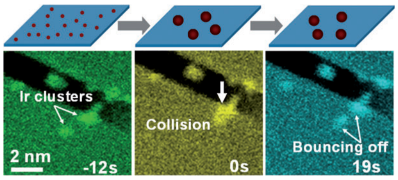


The electrophilic $[Ph_3PAu]NTf_2$ quickly diaurates aryl boronic acids providing stable geminally diaurated complexes (see example; yellow, Au; orange, P; blue, C) that have been spectroscopically, and in some cases crystallographically, characterized. Geminally diaurated arenes are putative intermediates in gold(I) catalysis and are analogues of Wheland intermediates of electrophilic aromatic substitutions.

Sinter-Resistant Catalysts

C. Aydin, J. Lu, N. D. Browning,
B. C. Gates* ______ **5929 – 5934**

A “Smart” Catalyst: Sinter-Resistant Supported Iridium Clusters Visualized with Electron Microscopy



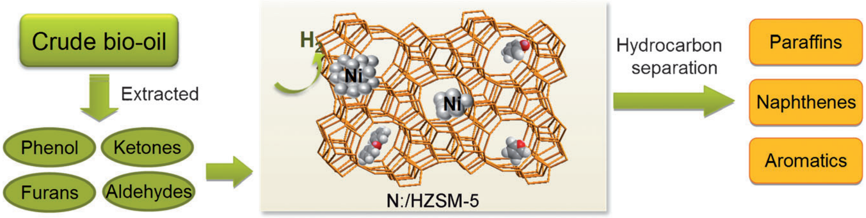
Like billiard balls: Atomic-scale observations by electron microscopy of supported iridium nanoclusters show that the nanoclusters aggregate to reach a critical diameter of approximately 1 nm and then resist further aggregation (see picture). The observations highlight the potential for this catalyst to assemble into clusters that may be nearly optimum for catalytic activity.

Biofuels

C. Zhao, J. A. Lercher* ______ **5935 – 5940**

Upgrading Pyrolysis Oil over Ni/HZSM-5 by Cascade Reactions

Front Cover

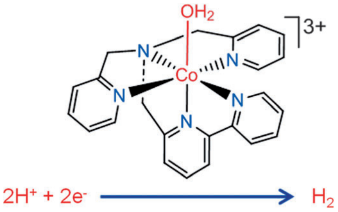


Bio-oil to hydrocarbon oil: An active, selective, and stable catalyst (Ni supported in zeolite HZSM-5) allows the conversion of a wide variety of C—O and C=O bonds in *n*-hexane-extracted pyrolysis oil into hydrocarbons through a cascade of hydrogenation, hydrolysis, dehydration, and dehydroaromatization reactions. Quantitative yields of C$_5$–C$_9$ gasoline-range hydrocarbons are obtained under mild conditions in water.

Hydrogen Evolution

W. M. Singh, T. Baine, S. Kudo, S. Tian,
X. A. N. Ma, H. Zhou, N. J. DeYonker,
T. C. Pham, J. C. Bollinger, D. L. Baker,
B. Yan, C. E. Webster,*
X. Zhao* ______ **5941 – 5944**

Electrocatalytic and Photocatalytic Hydrogen Production in Aqueous Solution by a Molecular Cobalt Complex

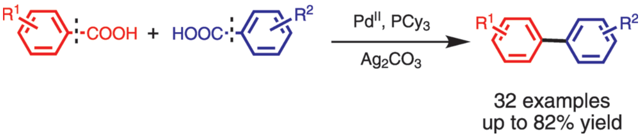


A mononuclear cobalt complex supported by a new type of pentadentate ligand catalyzed the evolution of hydrogen in purely aqueous solution (see picture). This cobalt complex could serve as both electrocatalyst and photocatalyst for efficient evolution of hydrogen.

Cross-Coupling

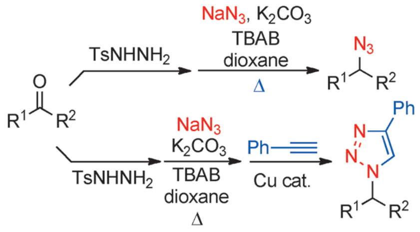
P. Hu, Y. Shang, W. Su* ______ **5945 – 5949**

A General Pd-Catalyzed Decarboxylative Cross-Coupling Reaction between Aryl Carboxylic Acids: Synthesis of Biaryl Compounds



Acid to acid: A general method has been developed for the synthesis of biaryl compounds through a decarboxylative cross-coupling reaction between two different (hetero)aryl carboxylic acids (see scheme). The use of a Pd^{II}/PCy$_3$ catalyst enables the cross-coupling reaction of electronically different or electronically similar aryl carboxylic acids. This method is compatible with substrates having nitro, cyano, fluoro, chloro, bromo, trifluoromethyl, and methoxy substituents.

Simple and direct: Aldehydes and ketones can be transformed into alkyl azides through a reductive coupling of the corresponding tosylhydrazones in a process that takes place simply in the presence of K_2CO_3, tetrabutylammonium bromide (TBAB), and NaN_3 (top of scheme). The application of this methodology followed by the Cu-catalyzed azide–alkyne cycloaddition allows the direct transformation of carbonyl compounds into triazoles (bottom of scheme).



Synthetic Methods

J. Barluenga,* M. Tomás-Gamasa,
C. Valdés* **5950 – 5952**

Reductive Azidation of Carbonyl Compounds via Tosylhydrazone Intermediates Using Sodium Azide

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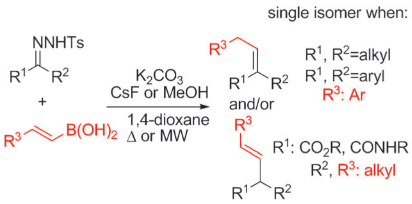
The partners decide: The C–C bond-forming reductive cross-coupling of alkenylboronic acids and tosylhydrazones takes place under mild reaction conditions without the need of a metal catalyst, thus giving rise to olefination-type products (see scheme). The position of the double bond in the product is determined by the structure of the coupling partners.



Synthetic Methods

M. C. Pérez-Aguilar,
C. Valdés* **5953 – 5957**

Olefination of Carbonyl Compounds through Reductive Coupling of Alkenylboronic Acids and Tosylhydrazones

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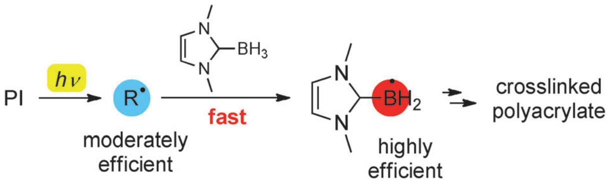

To protect and serve: The efficiency of Type I radical photoinitiators for acrylate polymerization is greatly increased by the presence of NHC-boranes. Conversion of the initially photogenerated radicals, R• (see scheme), into strongly nucleophilic NHC-boryl radicals, through hydrogen-atom transfer, gives a better matched radical for subsequent reaction with monomer, ensuring better initiation.

Photopolymerization

J. Lalevée,* S. Telitel, M. A. Tehfe,
J. P. Fouassier, D. P. Curran,
E. Lacôte* **5958 – 5961**

N-Heterocyclic Carbene Boranes Accelerate Type I Radical Photopolymerizations and Overcome Oxygen Inhibition

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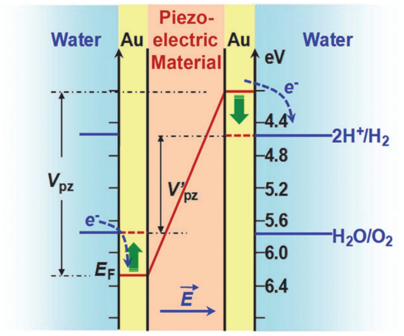


Piezocatalysis uses piezopotential to modulate charge carrier energetics (see picture), thus allowing the direct enhancement or suppression of electrochemical reactions that occur at a piezoelectric material/solution interface. Such a direct conversion of mechanical to chemical energy is shown by the electrochemical H_2 evolution that is achieved by straining a piezoelectric material in aqueous medium.

Piezocatalysis

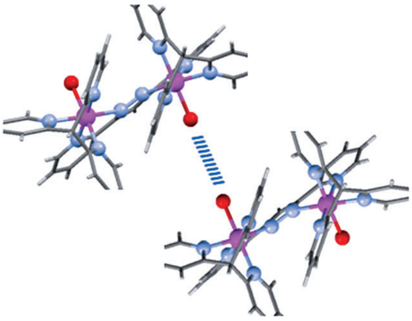
M. B. Starr, J. Shi,
X. D. Wang* **5962 – 5966**

Piezopotential-Driven Redox Reactions at the Surface of Piezoelectric Materials

Water Oxidation

S. Maji, L. Vigara, F. Cottone,
F. Bozoglian, J. Benet-Buchholz,
A. Llobet* ______ 5967 – 5970

Ligand Geometry Directs O–O Bond-Formation Pathway in Ruthenium-Based Water Oxidation Catalyst



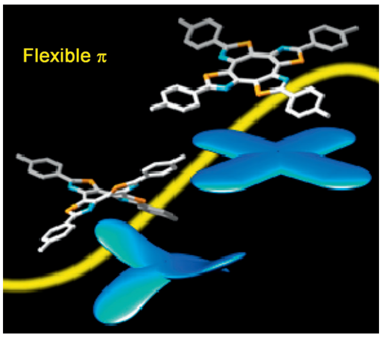
It takes two: A new dinuclear Ru-OH_2 complex has been prepared and serves as a water oxidation catalyst (see figure; O red, N lavender, Ru pink). Structural and kinetic analyses, as well as reactivity tests provide compelling evidence, showing that the crucial O–O bond-formation steps occur through a bimolecular I2M mechanism. Furthermore, this bimolecular interaction is demonstrated for the first time using ^{18}O-labeling experiments.

Cyclooctatetraene

K. Mouri, S. Saito,
S. Yamaguchi* ______ 5971 – 5975

Highly Flexible π-Expanded Cyclooctatetraenes: Cyclic Thiazole Tetramers with Head-to-Tail Connection

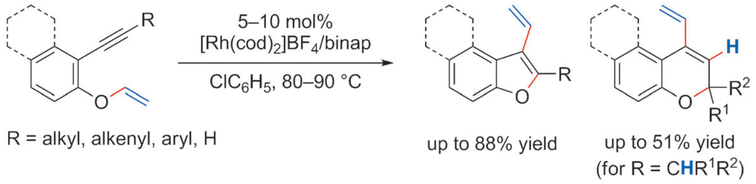
Flipping fast: Head-to-tail cyclic thiazole tetramers representing flexible π-expanded cyclooctatetraenes were designed and synthesized (see picture). The presence of fused thiazole rings in a head-to-tail arrangement leads to a strong columnar stacking of the shallow saddle-shaped π-conjugated molecules, an unusually low inversion barrier of 6.8 kcal mol^{-1}, and reduction-induced complete planarization to an aromatic ring system.



Organometallic Catalysis

N. Sakiyama, K. Noguchi,
K. Tanaka* ______ 5976 – 5980

Rhodium-Catalyzed Intramolecular Cyclization of Naphthol- or Phenol-Linked 1,6-Enynes Through the Cleavage and Formation of sp^2 C–O Bonds



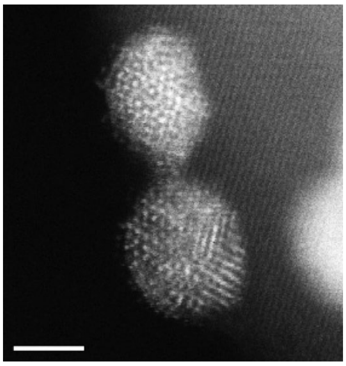
Put a ring on it: A cationic rhodium(I)/binap complex catalyzes the intramolecular cyclization reactions of naphthol- or phenol-linked 1,6-enynes to produce vinylnaphtho- or vinylbenzofurans and vinylnaphtho- or vinylbenzopyrans through the cleavage and formation of sp^2 C–O bonds. Mechanistic studies imply that the present cyclization reactions proceed through β-oxygen elimination from cationic rhodacycle intermediates.

Heterogeneous Catalysis

M. I. bin Saiman, G. L. Brett,
R. Tiruvalam, M. M. Forde, K. Sharples,
A. Thetford, R. L. Jenkins, N. Dimitratos,
J. A. Lopez-Sanchez, D. M. Murphy,
D. Bethell, D. J. Willock, S. H. Taylor,
D. W. Knight, C. J. Kiely,
G. J. Hutchings* ______ 5981 – 5985

Involvement of Surface-Bound Radicals in the Oxidation of Toluene Using Supported Au-Pd Nanoparticles

All bound up: Au-Pd nanoparticles having a mean particle size of 3–4 nm and supported on titania (see figure; scale bar 2 nm) exhibit high activity in the selective oxidation of aromatic hydrocarbons using *tert*-butyl hydroperoxide as an oxidant. The supported nanoparticles stabilize surface-bound radicals.

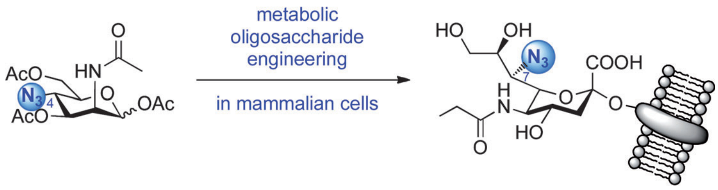


Sialic Acid Engineering

H. Möller, V. Böhrsch, J. Bentrop,
J. Bender, S. Hinderlich,*
C. P. R. Hackenberger* ____ 5986 – 5990

Glycan-Specific Metabolic Oligosaccharide Engineering of C7-Substituted Sialic Acids

Inside Cover

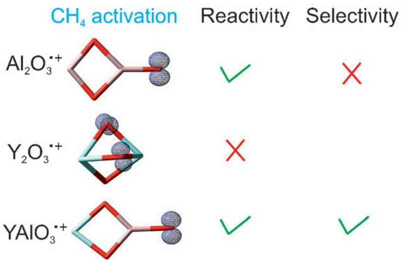


A new sialic acid in the house! A biosynthetic approach gives access to previously inaccessible C7 modifications of sialic acids in living cells. Metabolic incorporation of synthetically derived *N*-acetyl-4-azido-4-deoxymannosamine (see scheme) into glycans of mammalian cells and zebrafish larvae preserves the bioorthogonal functionality of its azido group for subsequent labeling with biophysical probes.

Methane Activation

J.-B. Ma, Z.-C. Wang, M. Schlangen,*
S.-G. He,* H. Schwarz* ____ 5991 – 5994

Thermal Reactions of $\mathrm{YAlO_3^{+\bullet}}$ with Methane: Increasing the Reactivity of $\mathrm{Y_2O_3^{+\bullet}}$ and the Selectivity of $\mathrm{Al_2O_3^{+\bullet}}$ by Doping



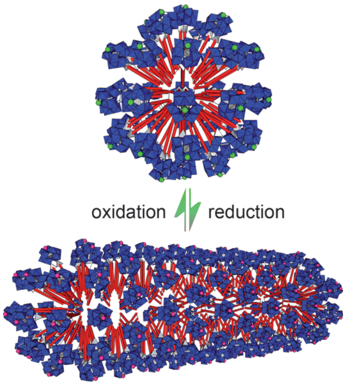
HAT in hand: The heteronuclear oxide cluster $\mathrm{YAlO_3^{+\bullet}}$ exhibits higher reactivity and selectivity than $\mathrm{Y_2O_3^{+\bullet}}$ and $\mathrm{Al_2O_3^{+\bullet}}$, respectively, in the reaction with methane by hydrogen-atom transfer (HAT) at room temperature (see scheme).

Self-Assembly

S. Landsmann, M. Wessig, M. Schmid,
H. Cölfen, S. Polarz* ____ 5995 – 5999

Smart Inorganic Surfactants: More than Surface Tension

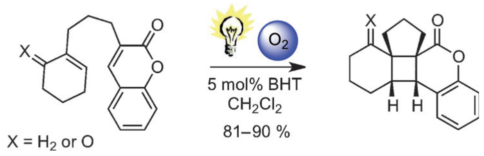
Hot under the surface: Surfactants with purely inorganic head groups, comprising a ruthenium-substituted polyoxotungstate cluster, are used to unlock the enormous potential of a synergistic combination of surfactant self-assembly and stimuli-responsive properties. The system can dynamically respond to a chemical trigger (such as a change in micelle shape; see scheme), and could lead to new applications for surfactants in light harvesting.



Photochemistry with Visible Light

D. P. Kranz, A. G. Griesbeck,* R. Alle,
R. Perez-Ruiz, J. M. Neudörfl, K. Meerholz,
H.-G. Schmalz* ____ 6000 – 6004

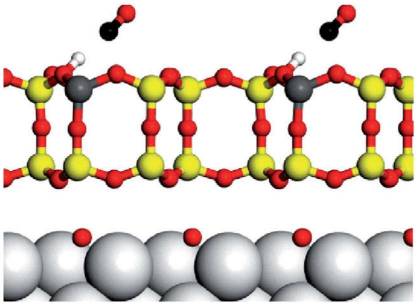
Molecular Oxygen as a Redox Catalyst in Intramolecular Photocycloadditions of Coumarins



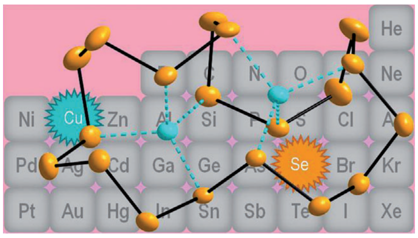
Oxygen as a catalyst! While oxygen is usually excluded in nonoxidative photochemical reactions, the photocycloaddition of 3-(alk-4-en-1-yl)-substituted coumarins greatly benefits from the presence of O_2, which was shown to act as a redox catalyst, preferentially in combination with the common antioxidant 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT).

Modeling Zeolites

Flat pore models: Thin, well-defined aluminosilicate films with tetrahedral $[SiO_{4/2}]$ and $[AlO_{4/2}^{-}]$ building blocks that are weakly bound to an underlying metal support contain highly acidic bridging OH species, which exhibit H–D exchange (see picture; Si yellow, O red, Al gray, C black, H white). These films are a model system for surface-science studies of the inner walls of zeolite pores.



Selenium Rings



Freshly prepared red selenium and the copper(I) reagent $[Cu(1,2\text{-}F_2C_6H_4)_2][A]$ are the key to the salts $[Cu_2Se_{19}][A]_2$ and $[Cu_2Se_{19}][A]_2{\cdot}0.5\,Na[A]$ ($[A] = [Al(OR^F)_4]$, $R^F = C(CF_3)_3$), which provides the first structurally characterized E_{19} ring of any element E. The unusual $[Cu_2Se_{19}]^{2+}$ ion contains two Cu^+ ions that stabilize the C_2-symmetric Se_{19} ring.

Supporting information is available on www.angewandte.org (see article for access details).

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