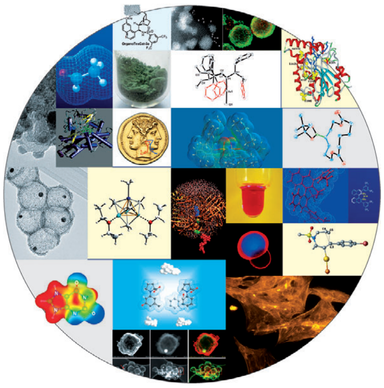
Some of the most important chemical discoveries …



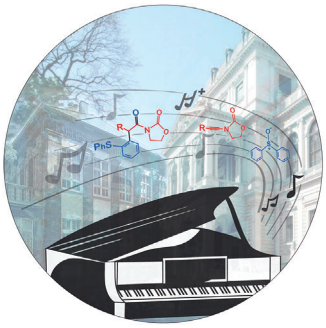
… of the last 100 years were made at the Max-Planck-Institut für Kohlenforschung (MPI) in Mülheim an der Ruhr, which was founded in 1914—100 years ago—as the Kaiser-Wilhelm-Institut für Kohlenforschung. A look at history illustrates the scientific potential of the Mülheim basic research: In 1925, F. Fischer and H. Tropsch filed a patent for the Fischer–Tropsch synthesis—gasoline from coal. The low-pressure approach to polyethylene was patented in 1953 by K. Ziegler, H. Breil, E. Holzkamp, and H. Martin. Ziegler was awarded the Nobel Prize in 1963 for this work. The decaffeination of coffee by supercritical carbon dioxide was patented in 1970 by K. Zosel. This Issue, starting with an Editorial by B. List on page 8528 ff., contains contributions from researchers, who have had a close connection in one way or another with this extraordinary Institution during their scientific careers. A summary of the history of the "KoFo-MPI" is given in the Essay by M. Reetz on page 8562 ff.

Heterogeneous Catalysis

N. López, J. Pérez-Ramírez, and co-workers show on page 8628 ff. that HBr doping of the rutile TiO_2 surface generates impurity levels with electrons that can be injected into or recovered from the reactants at the right energies, transforming the catalytically inert semiconductor into an active catalyst.

Redox Catalysis

In their Communication on page 8718 ff., N. Maulide et al. describe the catalytic redox-neutral arylation of ynamides with aryl sulfoxides, which is illustrated by the harmonious catalysis of a proton.



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Editorial

"... In this special issue of Angewandte Chemie, which is indeed very special for us, you as a reader should get an impression of what, in our opinion, constitutes the research in and around the Max-Planck-Institut für Kohlenforschung. You will notice the diversity of the research topics that are covered by researchers at the Institute ..."
Read more in the Editorial by Benjamin List.

B. List* **8528–8530**

Catalytic Processes that Changed the World: 100 Years Max-Planck-Institut für Kohlenforschung

Front Cover

Back Cover

Service

Spotlight on Angewandte's Sister Journals ***8546–8549***

Author Profile

"My motto is never give up!
In a spare hour, I read a newspaper ..."
This and more about Graham J. Hutchings can be found on page 8550.

Graham J. Hutchings **8550–8551**


F. Schüth

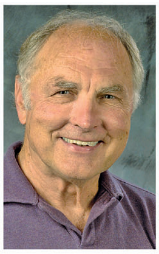

W. Thiel


G. Wilke


M. T. Reetz


A. Corma


M. E. Davis


G. D. Stucky


S. L. Buchwald

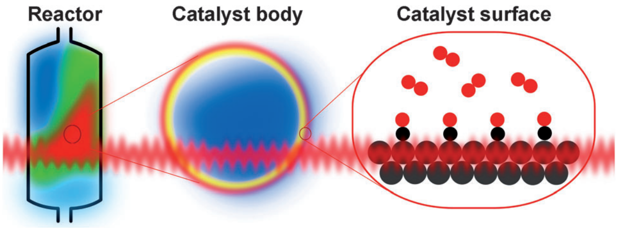

B. M. Trost


M. Beller

News

Highlights

Heterogeneous Catalysis



Diffraction at hard work: Modern heterogeneous catalysis would benefit from a multiscale science approach bridging the molecular world with the macroscopic world. Because of recent breakthroughs in X-ray diffraction methods, including the surface X-ray diffraction of atomically flat model catalysts, X-ray diffraction tomography of catalyst bodies, and X-ray profiling of an active catalyst in a chemical reactor, such an approach is now within reach.

For the USA and Canada:
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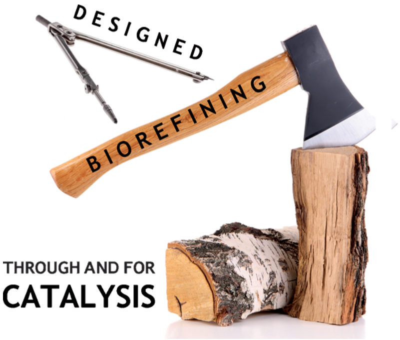
Renewable Resources



Catalytic biorefining: Beyond the deconstruction of plant biomass, emerging processes for catalytic biomass fractionation are directed towards rationally designing the properties of the isolated biomass components *through* and *for* catalysis. The full potential of catalysis in the conversion of the isolated fractions into chemicals and fuels can thus be exploited.

Essays

100 Years of Catalysis

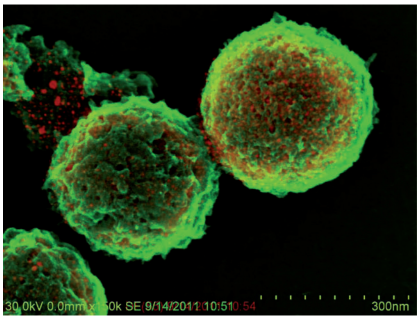
Catalysis pure: This Essay is an account of the institutional and scientific development of the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr (Germany), which is the successor to the Kaiser-Wilhelm-Institut für Kohlenforschung founded in 1914. It is an institute that has focused on catalysis for 100 years. Key historical events, organizational changes, and research highlights of four major periods are featured.

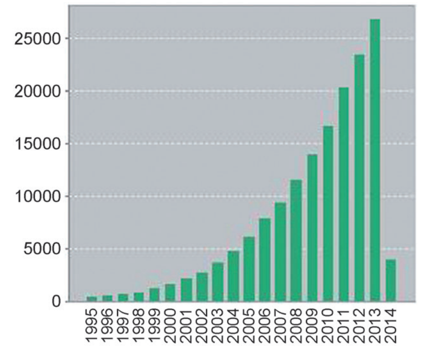
Catalysis in Mülheim

Divining rod: Natural product synthesis often serves as a divining rod in our search for new and useful catalytic reactivity. This personal account—written in honor of the Max-Planck-Institut für Kohlenforschung on the occasion of its 100th anniversary—summarizes the major lines of research pursued in the author's laboratory, which show how total synthesis and research into basic organometallic chemistry cross-fertilize each other.

Heterogeneous Catalysis

Down to the last detail: Nanostructured solid catalysts were already known in the early 20th century, but their exact structure was unclear. Nowadays, the arrangement of atoms and particles in solids can be manipulated and analyzed down to the atomic scale (see image). The use of specific highly active catalysts enables industrially relevant reactions to be performed at room temperature.

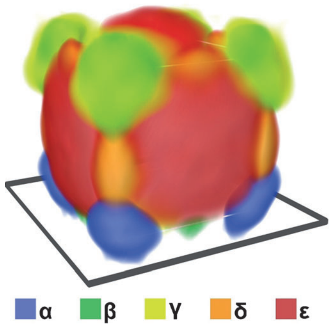




The explosive growth of computational catalysis over the past two decades is reflected by the exponentially increasing number of citations. The Essay traces the historical development, illustrates the current state, and offers comments on the future perspectives of this field.

Computational Chemistry

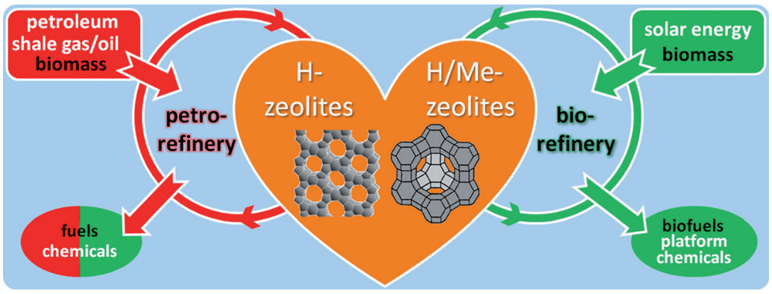
Modern electron microscopy permits the acquisition of multi-dimensional data sets that combine 3D real space morphology with chemical, temporal, and crystallographic information providing new insights into the physico-chemical behavior of materials at the nanoscale.



Electron Microscopy

The perfect catalyst: The advances towards the ability to design a catalyst from first principles are explored. Aspects of computational chemistry as well as the kinetics and physical state of the reactive catalyst are discussed.

Heterogeneous Catalysis



Approved catalysts for fuels of the future: Transition from petroleum- to biomass-based fuel economy will require new conversion strategies. This Essay describes how recent developments in zeolite synthesis and modification allow adapting zeolite properties to achieve selective conversion of biomass compounds.

Zeolites in Biorefineries

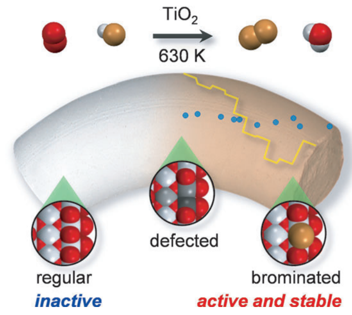
Communications

Defects in Catalysis

M. Moser, I. Czekaj, N. López,*
J. Pérez-Ramírez* __________ **8628 – 8633**

The Virtue of Defects: Stable Bromine Production by Catalytic Oxidation of Hydrogen Bromide on Titanium Oxide

Frontispiece



Who wants to be perfect? Rutile TiO_2 has a limited use in heterogeneous catalysis owing to its inertness and its relatively low surface area. The in situ generation of defect states on the rutile surface enables the dissociation of molecular oxygen, transforming this semiconductor into a highly active, stable, and cost-effective catalyst. It catalyzes the oxidation of HBr to Br_2, an important reaction for halogen-mediated alkane functionalization processes.

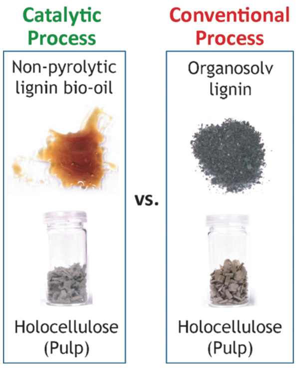
Heterogeneous Catalysis

P. Ferrini, R. Rinaldi* _____ **8634 – 8639**

Catalytic Biorefining of Plant Biomass to Non-Pyrolytic Lignin Bio-Oil and Carbohydrates through Hydrogen Transfer Reactions

Inside Cover

Lignin finds its true destiny: A catalytic biorefining method results in the isolation of depolymerized lignin, that is, a non-pyrolytic lignin bio-oil, in addition to pulps that are amenable to enzymatic hydrolysis. The lignin bio-oil is highly susceptible to hydrogenation under mild conditions, and therefore, a unique pathway for lignin valorization by heterogeneous catalysis has been established.

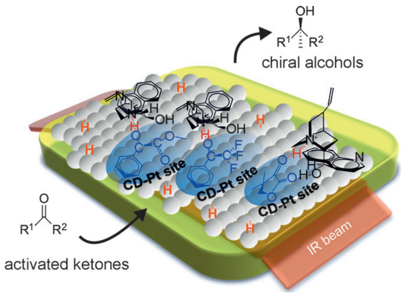


Asymmetric Catalysis

F. Meemken, K. Hungerbühler,
A. Baiker* __________ **8640 – 8644**

Monitoring Surface Processes During Heterogeneous Asymmetric Hydrogenation of Ketones on a Chirally Modified Platinum Catalyst by Operando Spectroscopy

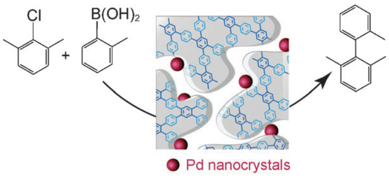
Watching the working catalyst: Surface processes occurring at the catalytic chiral surface of a cinchona-modified Pt catalyst during the asymmetric hydrogenation of activated ketones have been monitored by attenuated total reflection IR spectroscopy (see picture). Fundamental information about this catalytic system could be gained.



Polymeric Catalysts

F. Wang, J. Mielby, F. H. Richter,
G. H. Wang, G. Prieto, T. Kasama,
C. Weidenthaler, H.-J. Bongard,
S. Kegnæs, A. Fürstner,
F. Schüth* __________ **8645 – 8648**

A Polyphenylene Support for Pd Catalysts with Exceptional Catalytic Activity

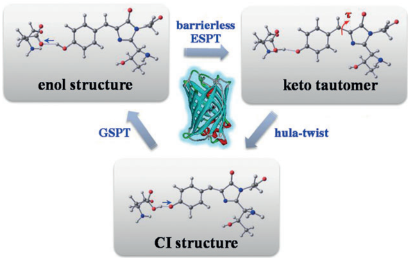


Support with benefits: A composite catalyst is synthesized by palladium-catalyzed Suzuki coupling which directly results in formation of palladium nanoparticles confined to a porous polyphenylene network. A polyphenylene support serves as an excellent platform for metal-catalyzed reactions, which are typically carried out under homogeneous conditions.

GFP Photochemistry

Q. Zhang, X. Chen,* G. Cui, W. Fang,
W. Thiel* ________ **8649 – 8653**

Concerted Asynchronous Hula-Twist Photoisomerization in the S65T/H148D Mutant of Green Fluorescent Protein

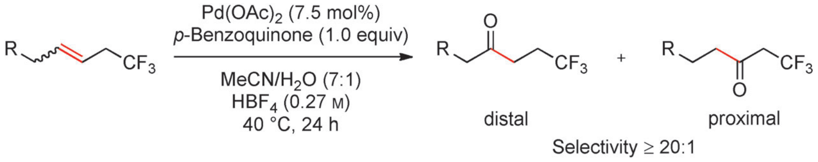


GFP mutant likes the hula-twist: QM/MM calculations show that the protein environment makes the S65T/H148D green fluorescent protein (GFP) double mutant adopt the concerted asynchronous hula-twisting pathway for isomerization (see picture), instead of the one-bond flip favored in its absence. Hydrogen out-of-plane motion is for the first time found to play an important role in GFP deactivation.

Synthetic Methods

M. M. Lerch, B. Morandi, Z. K. Wickens,
R. H. Grubbs* ________ **8654 – 8658**

Rapid Access to β-Trifluoromethyl-Substituted Ketones: Harnessing Inductive Effects in Wacker-Type Oxidations of Internal Alkenes

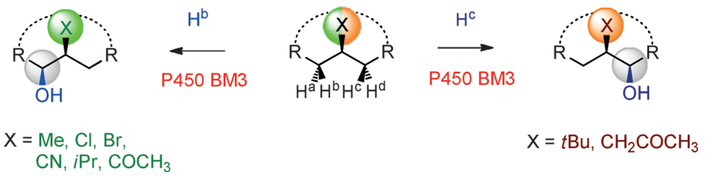


Synthetically highly desirable β-trifluoromethyl-substituted ketones can be rapidly accessed by a trifluoromethyl-directed Wacker oxidation starting from alkenes bearing an allylic trifluoromethyl group (see scheme). This effect seems to be dominantly inductive and can override coordinative effects. The reaction has a broad substrate scope and affords products in high yields and very high regioselectivity.

Biocatalysis

G.-D. Roiban, R. Agudo,
M. T. Reetz* ________ **8659 – 8663**

Cytochrome P450 Catalyzed Oxidative Hydroxylation of Achiral Organic Compounds with Simultaneous Creation of Two Chirality Centers in a Single C—H Activation Step

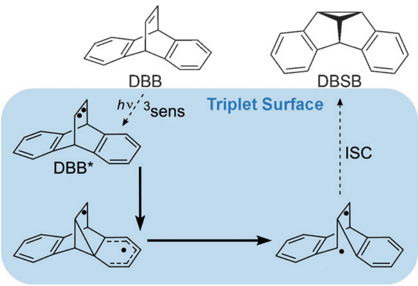


Two birds with one stone: Two new centers of chirality are created by the cytochrome P450 catalyzed regio-, diastereo-, and enantioselective oxidative hydroxylation of appropriate achiral compounds. When using either wild type cytochrome P450 BM3 or mutants generated by directed evolution, a high preference for one of the four stereotopic H atoms is observed depending on the nature of the X moiety in the substrate.

Molecular Dynamics

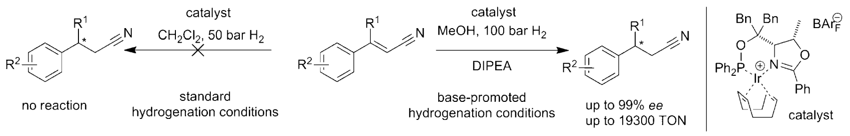
G. Jiménez-Osés, P. Liu, R. A. Matute,
K. N. Houk* ________ **8664 – 8667**

Competition Between Concerted and Stepwise Dynamics in the Triplet Di-π-Methane Rearrangement



Once in a lifetime: The molecular dynamics of the triplet-state Zimmerman di-π-methane rearrangement of dibenzobarrelene (DBB) were computed. All productive quasiclassical trajectories involve sequential formation and cleavage of C—C bonds and an intermediate with lifetimes ranging from 13 to 1160 fs. Such short lifetimes indicate the nonstatistical nature of the reaction mechanism. DBSB = dibenzosemibullvalene, ISC = intersystem crossing.

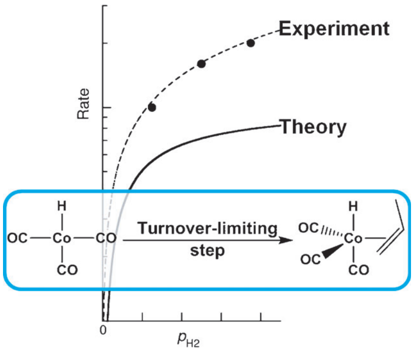
Asymmetric Hydrogenation



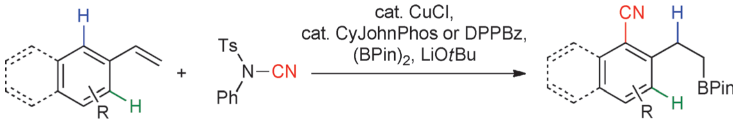
The base makes the difference. Addition of *N,N*-diisopropylethylamine (DIPEA) or the presence of a basic counterion dramatically enhance the activity of iridium catalysts in the asymmetric hydrogenation of α,β-unsaturated nitriles, a substrate class for which no suitable catalysts were available before. Under these conditions a cyano-substituted C=C bond can be selectively reduced, leaving less electrophilic C=C bonds intact.

Theory of Catalysis

Cobalt bottlenecks: Density functional theory, coupled-cluster theory, and transition state theory are used to build a computational model of the kinetics of phosphine-free cobalt-catalyzed hydroformylation and hydrogenation of alkenes. The model provides very good agreement with experiment (see picture), and enables the factors that determine the selectivity and rate of catalysis to be established. The turnover rate is mainly determined by the alkene coordination step.

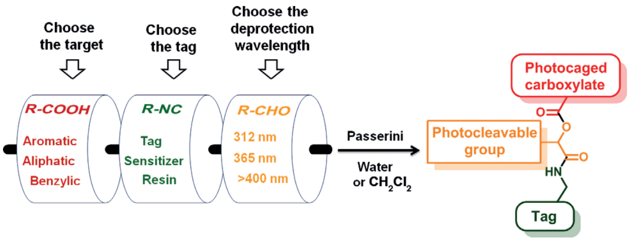


C–H Activation



Reaction combo: A combined copper-catalyzed hydroborylation/*ortho* C–H cyanation of vinylarenes is described, thus allowing the selective functionalization of vinylarenes and featuring unique site selectivity. The reaction leads to *ortho*-selective C–H functionalization of arenes and anti-Markovnikov hydrofunctionalization of the pendant olefin (see scheme; Pin = pinacolato, Ts = 4-toluenesulfonyl).

Photochemistry

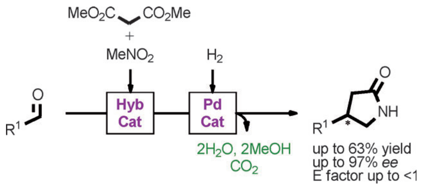


Mix and match: The multicomponent Passerini reaction is used for the preparation of photocaged carboxylic acids, both in dichloromethane and water. Judicious choice of the aldehyde allows tuning of the deprotection wavelength and the preparation of orthogonally protected products. The isocyanide component may be used for immobilization on a solid support or introduction of either a reactive tag or a photosensitizer.

Heterogeneous Domino Catalysis

A. Leyva-Pérez, P. García-García,* A. Corma* ——— **8687 – 8690**

Multisite Organic–Inorganic Hybrid Catalysts for the Direct Sustainable Synthesis of GABAergic Drugs

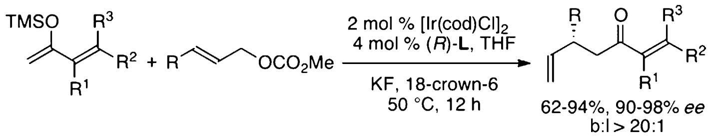


Seven steps in two pots: Organic–inorganic hybrid catalysts have been prepared and applied in a new general, practical, and flexible synthetic procedure toward industrially relevant GABA derivatives. The domino sequence is composed of seven chemical transformations which are performed in two one-pot reactions. The method produces both enantiomeric forms of the product in high enantiopurity as well as the racemate in good yields.

Asymmetric Catalysis

M. Chen, J. F. Hartwig* —— **8691 – 8695**

Iridium-Catalyzed Enantioselective Allylic Substitution of Unstabilized Enolates Derived from α,β-Unsaturated Ketones

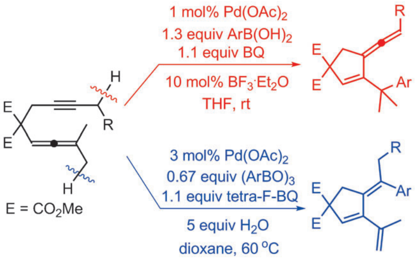


Highly selective: An Ir-catalyzed enantioselective allylic substitution reaction of unstabilized silyl enolates derived from α,β-unsaturated ketones was developed. Reaction with a variety of allylic carbonates gave allylated products in good yields with high enantioselectivities and excellent branched-to-linear selectivities. The synthetic utility was demonstrated in the synthesis of an anticancer agent, TEI-9826.

Homogeneous Catalysis

T. Bartholomeyzik, J. Mazuela, R. Pendrill, Y. Deng,* J.-E. Bäckvall* —— **8696 – 8699**

Palladium-Catalyzed Oxidative Arylating Carbocyclization of Allenynes: Control of Selectivity and Role of H_2O

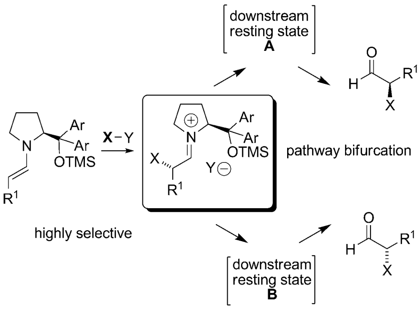


Selective protocols are described for the carbocyclization/arylation of allenynes using arylboronic acids that allow for the formation of either arylated vinylallenes or arylated trienes. Formation of the former product is promoted by the use of $BF_3{\cdot}Et_2O$ whereas the latter product is selectively formed when water is used as an additive. Water plays a crucial role for the product distribution.

Organocatalysis

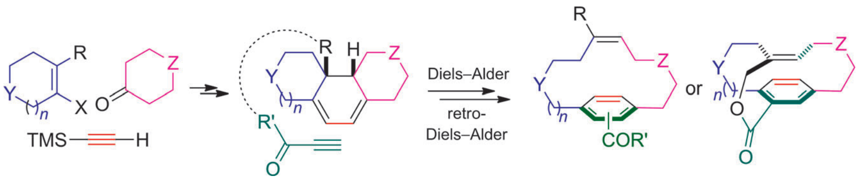
J. Burés, P. Dingwall, A. Armstrong,* D. G. Blackmond* ——— **8700 – 8704**

Rationalization of an Unusual Solvent-Induced Inversion of Enantiomeric Excess in Organocatalytic Selenylation of Aldehydes



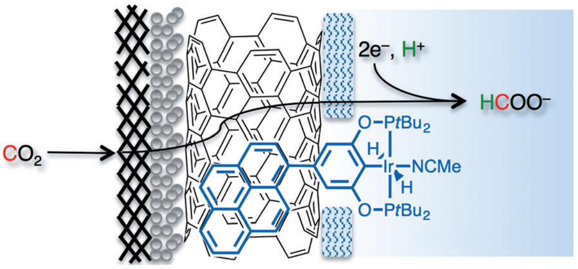
Off the beaten path: Studies of an unusual inversion of the sense of enantioselectivity for the selenylation of aldehydes catalyzed by a diphenylprolinol ether catalyst provides support for a mechanistic concept beyond the simple steric model developed for enamine catalysis in these systems. A general role for downstream intermediates in selectivity outcomes in organocatalysis is discussed. TMS = trimethylsilyl.

Molecular Diversity



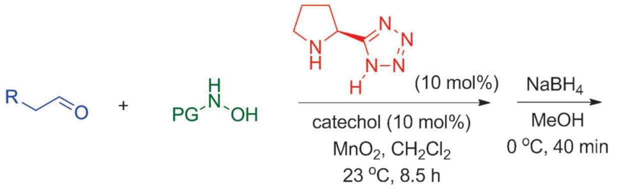
An efficient, modular, and simple access to new diverse functionalized [*n*]paracyclophanes, incorporating heteroatoms and structural features such as aryl ethers, biaryl subunits, or lactams, as well as original cage architectures, has been developed from readily available building blocks. The approach relies on sequential Diels–Alder/retro-Diels–Alder reactions.

CO_2 Reduction



Zapping CO_2 interfacially: An iridium pincer dihydride catalyst (in 0.1 M $NaHCO_3$) was immobilized on a gas diffusion electrode. The catalytic system is efficient, selective, and stable for electrochemical reduction of CO_2 to formate in water.

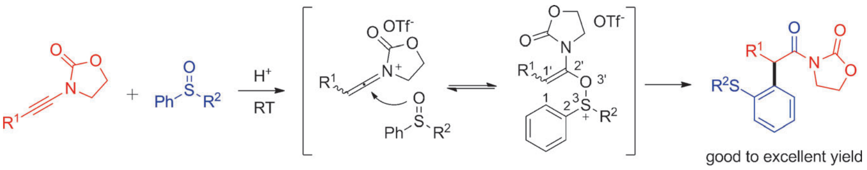
Organocatalysis



Sturdy as it gets: A highly enantioselective, robust, and scalable method for the synthesis of β-hydroxyamino alcohols was achieved by using the title reaction. MnO_2 serves as the oxidant and catechol as the Brønsted acid additive. PG = protecting group.

Redox Catalysis

Inside Back Cover

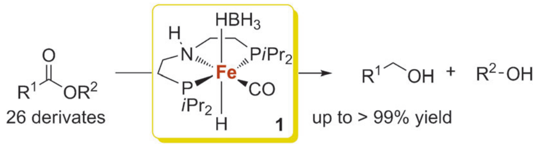


Playing a neutral game: A Brønsted acid catalyzed redox-neutral arylation of ynamides with aryl sulfoxides is described. A broad range of ynamides were converted into the corresponding α-arylated oxazolidinones in good to excellent yields under mild conditions and in an atom-economic fashion. Tf = trifluoromethylsulfonyl.

Iron Catalysis

S. Werkmeister, K. Junge, B. Wendt,
E. Alberico, H. Jiao, W. Baumann,
H. Junge, F. Gallou,
M. Beller* ______ **8722 – 8726**

Hydrogenation of Esters to Alcohols with a Well-Defined Iron Complex

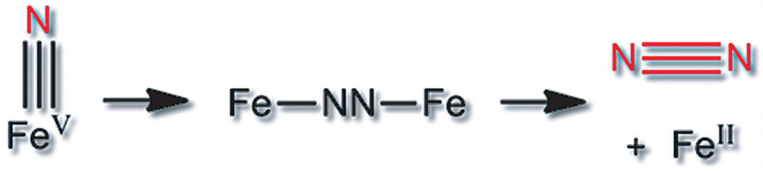


A brilliant progressIRON: A novel and efficient catalyst system based on iron complex **1** has been developed for the hydrogenation of various aromatic and aliphatic carboxylic acid esters as well as lactones towards the corresponding alcohols. The reaction is postulated to proceed by an outer-sphere mechanism.

Bioinorganic Chemistry

O. Krahe, E. Bill, F. Neese* . **8727 – 8731**

Decay of Iron(V) Nitride Complexes By a N–N Bond-Coupling Reaction in Solution: A Combined Spectroscopic and Theoretical Analysis



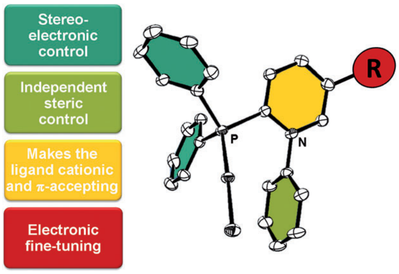
Always look on the bright azide of life: the qualitative formation of dinitrogen results from the decay of Fe^{V} nitride complexes and is investigated by a combination of spectroscopy, spectrometry, and theory. New insight is obtained in the photolysis of iron azide complexes, which is crucial for the formation of iron nitrides.

Cationic Phosphines

H. Tinnermann, C. Wille,
M. Alcarazo* ______ **8732 – 8736**

Synthesis, Structure, and Applications of Pyridiniophosphines

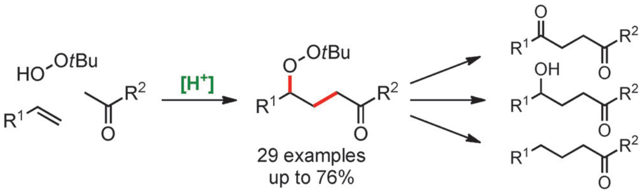
Be positive! Pyridinium-substituted phosphines carry a positive charge directly attached to the phosphorus atom. This makes them weak σ-donor but excellent π-acceptor ligands. Their synthesis and their remarkable effect in Pt and Au catalysis are described.



Synthetic Methods

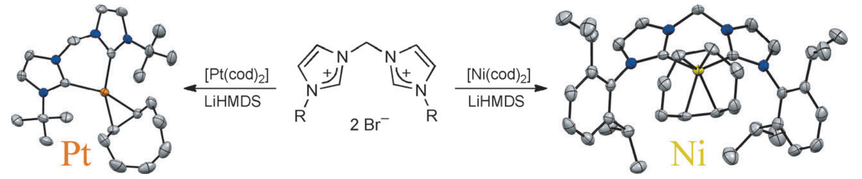
B. Schweitzer-Chaput, J. Demaerel,
H. Engler, M. Klussmann* _ **8737 – 8740**

Acid-Catalyzed Oxidative Radical Addition of Ketones to Olefins



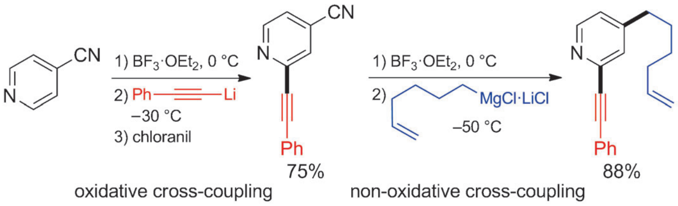
A radical combination: A multicomponent radical addition of unactivated ketones and hydroperoxide to styrenes under Brønsted acid catalysis provides a range of γ-peroxyketones. The products can be further transformed into 1,4-diketones, homoaldol compounds, and alkyl ketones. The formation of radicals is believed to proceed via thermally labile alkenylperoxides, which are generated in situ.

NHC Complexes



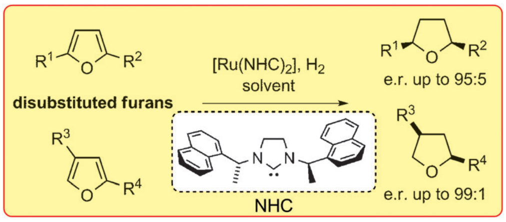
Adjusting the bite: d^{10}-ML_2 fragments are well known to activate unreactive bonds by oxidative addition. Starting from lithium carbene adducts formed in situ, nickel and platinum olefin complexes of such fragments bearing chelating bis-NHCs were synthesized. Combining these strong electron donors with the bent coordination geometry enforced by chelation opens interesting perspectives for bond-activation chemistry and catalysis.

BF_3-Mediated Coupling



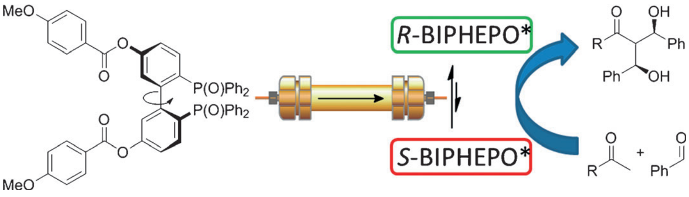
Oxidative or non-oxidative—That is the question! Pyridines bearing a substituent at position 4 readily undergo a BF_3-mediated oxidative coupling at position 2 with a wide range of alkynyllithium compounds. In contrast, 4-cyano- or 4-chloropyridines undergo a novel BF_3-mediated cross-coupling at position 4 with alkylmagnesium reagents. The combination of the two transition-metal-free procedures allows the preparation of a broad range of pyridines.

Asymmetric Hydrogenation



Pump it up! An asymmetric hydrogenation of disubstituted furans has been developed by using a Ru-NHC based catalyst system (NHC = N-heterocyclic carbene). This reaction converts flat furans into enantioenriched tetrahydrofurans of relevance in biology and material science.

Tropos Organocatalyst



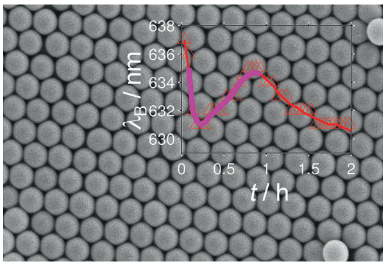
Deracemization does the trick: The catalytic chiral resolution of tropos biarylphosphineoxides is combined with their high stereoinduction in asymmetric double-aldol-additions. The transient diastereomeric interaction of the modified biarylphosphineoxide was maximized by molecular design, which leads to an unusually high deracemization during HPLC.

Colloidal Crystals

M. Muldarisnur, F. Marlow* **8761 – 8764**

Observation of Nano-Dewetting in Colloidal Crystal Drying

Short breath: The continuous shrinkage of a colloidal crystal during drying is spontaneously interrupted several minutes after starting the drying. The system seems to take a breath before it shrinks monotonously until its final state after about one day. This short period becomes visible by a short red-shift of the Bragg peak characterizing the lattice constant.

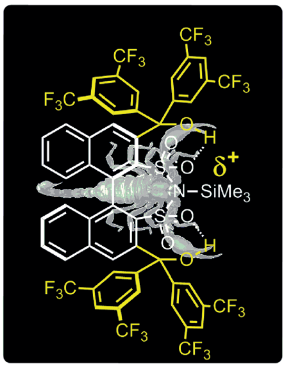


Organocatalysis

L. Ratjen, M. van Gemmeren, F. Pesciaioli, B. List* **8765 – 8769**

Towards High-Performance Lewis Acid Organocatalysis

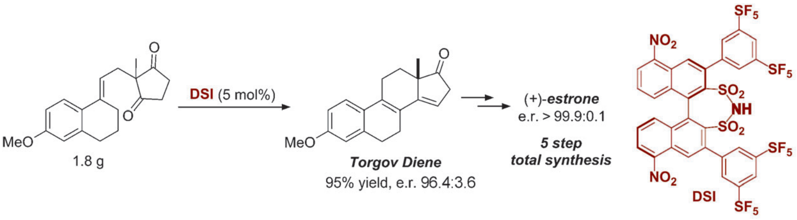
Ready to attack! The combination of Lewis acid organocatalysis and internal hydrogen-bond assistance was used to develop a new type of highly active disulfonimide catalyst. The increased Lewis acidity was documented by activity comparisons and theoretical investigations. The potential of the hydrogen-bond-assisted disulfonimide catalyst was demonstrated by its application in an enantioselective transformation.



Organocatalyis

S. Prévost, N. Dupré, M. Leutzsch, Q. Wang, V. Wakchaure, B. List* **8770 – 8773**

Catalytic Asymmetric Torgov Cyclization: A Concise Total Synthesis of (+)-Estrone

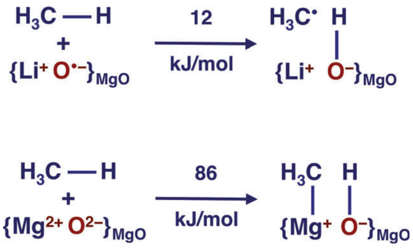


A short circuit: An asymmetric Torgov cyclization, catalyzed by a novel, highly Brønsted acidic dinitro-substituted disulfonimide, is described. The reaction delivers the Torgov diene and various analogues with excellent yields and enantioselectivity. The method was applied in a very short synthesis of (+)-estrone.

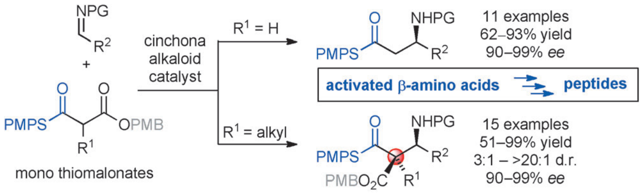
C–H Activation on MgO

K. Kwapien, J. Paier, J. Sauer,* M. Geske, U. Zavyalova, R. Horn,* P. Schwach, A. Trunschke,* R. Schlögl **8774 – 8778**

Sites for Methane Activation on Lithium-Doped Magnesium Oxide Surfaces

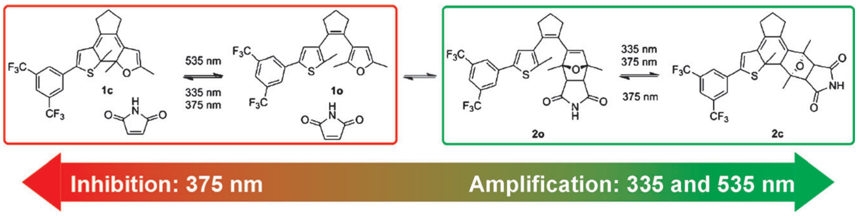


The energy barriers for methane activation by hydrogen abstraction at oxygen radical sites are unrealistically low. C–H bonds can also heterolytically add onto a regular MgO ion pair at morphological defects such as steps and corners. Release of methyl radicals into the gas phase will happen only in the presence of O_2.



PG=protecting group, PMP=p-methoxyphenyl, PMB=p-methoxybenzyl

Thioesters on the rise: β-Amino thioesters with tertiary and even quaternary stereogenic centers can be formed with high diastereo- and enantioselectivities from Mannich reactions with monothiomalonates in the presence of catalytic amounts of cinchona alkaloids. The synthetic value of the β-amino thioesters as preactivated β-amino acids was, for example, shown in coupling-reagent-free peptide synthesis.



Remote-controlled equilibrium: Gating both sides of a reversible covalent Diels–Alder reaction by a photoswitch allows control over the connection and disconnection of two chemical entities and shifting of their equilibrium by light. This approach should prove particularly powerful when designing dynamic cross-linked polymers and for reversible covalent functionalization of sp^2-hybridized carbon allotropes, such as graphene and carbon nanotubes.

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

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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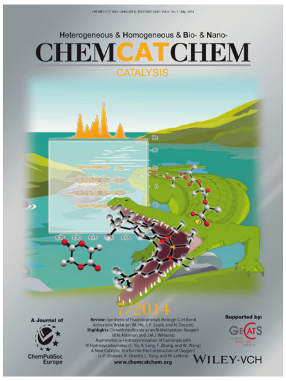

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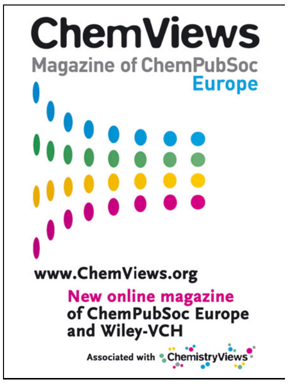

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