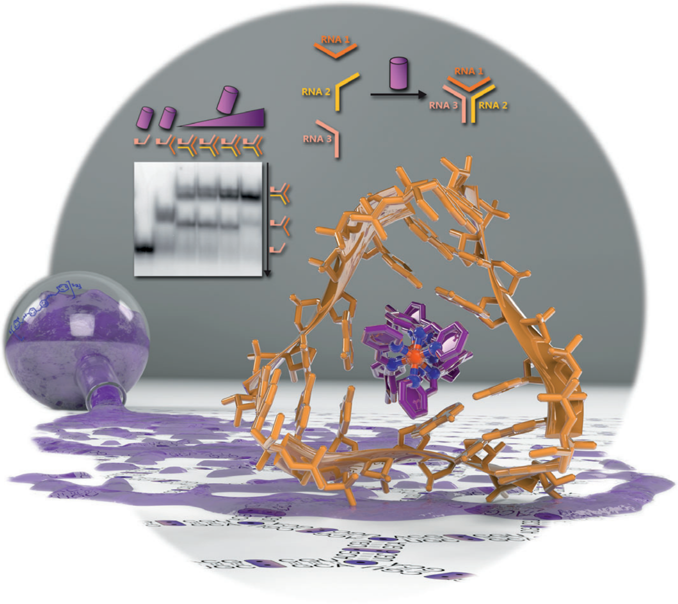
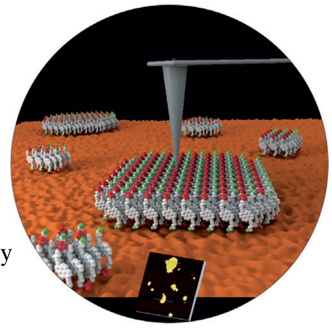
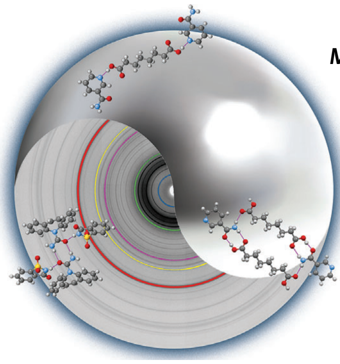
Recognition and stabilization ...



… of an RNA three-way junction by a supramolecular di-iron(II) cylindrical complex is described by R. K. O. Sigel, B. Spingler, M. J. Hannon, E. Freisinger et al. in their Communication on page 11513 ff. This potential anti-cancer metal-based drug fits perfectly into the central RNA core and stabilizes this architecture in the solid state as well as under native gel conditions. (Cover picture: Joachim Schnabl.)

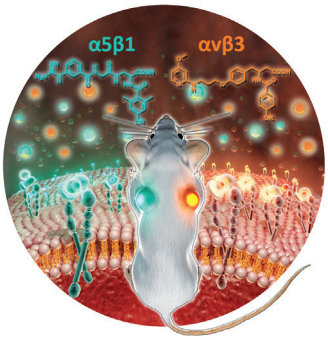
Supramolecular Polymers
AFM shows that amphiphilic pyrene trimers self-assemble into 2D, supramolecular sheet-like structures. R. Häner and co-workers report in their Communication on page 11488 ff. that the fluorescence properties of these structures are significantly changed by the self-assembly process.





Mechanochemistry
T. Friščić and co-workers describe in their Communication on page 11538 ff. how ball-milling reactions of organic pharmaceutical solids can be monitored in situ and in real time with high-energy X-rays.

Tumor Imaging
α5β1 or αvβ3 subtype-selective integrin antagonists can be functionalized with NODAGA. In their Communication on page 11656 ff., H. Kessler and co-workers show these peptidomimetics make in vivo tumor imaging possible by positron emission tomography (PET).



How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

Service

Author Profile

"I admire people with strong determination and persistence.
My favorite musician is the violinist Jascha Heifetz …"
This and more about Chi-Huey Wong can be found on page 11452.

News

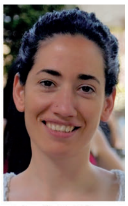

T. Torres


M. Solà


F. P. Cossío


T. Rojo


J. Alemán


N. Crivillers


J. L. Delgado


J. Solla Gullón


G. Erker


J.-F. Nierengarten


A. J. L. Pombeiro


F. Zerbetto

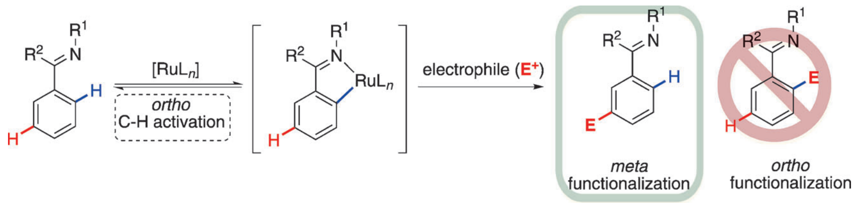
Books

Highlights

C–H Activation

F. Juliá-Hernández, M. Simonetti,
I. Larrosa* ——————— **11458 – 11460**

Metalation Dictates Remote Regioselectivity: Ruthenium-Catalyzed Functionalization of *meta* C_{Ar}–H Bonds



Remote control: The title reaction is effective for the sulfonation and alkylation of arenes bearing directing groups. Initial *ortho* metalation of the substrate forms an intermediate which does not evolve towards functionalization at the C–M bond. Instead, the ruthenium catalyst acts as a strong electron-donating group, thus directing a remote electrophilic attack.

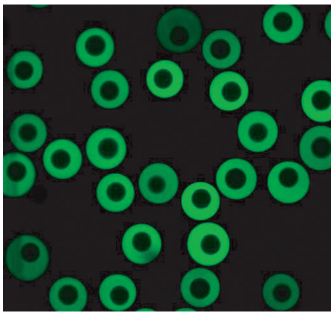
Minireviews

Microgels

S. Seiffert* ——————— **11462 – 11468**

Small but Smart: Sensitive Microgel Capsules

Sensitive microgels consist of micrometer-scale swollen polymer networks that can be actuated by external stimulation. To make this truly useful for encapsulating additives, it is necessary to control the microgel size, shape, and loading; this is possible with microfluidic particle templating.



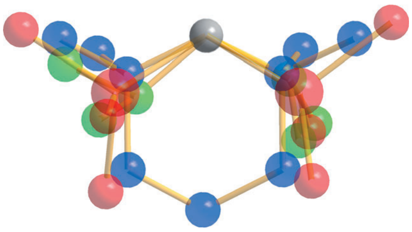
Reviews

Alkali-Metal Amides

R. E. Mulvey,*
S. D. Robertson* ——————— **11470 – 11487**

Synthetically Important Alkali-Metal Utility Amides: Lithium, Sodium, and Potassium Hexamethyldisilazides, Diisopropylamides, and Tetramethylpiperidides

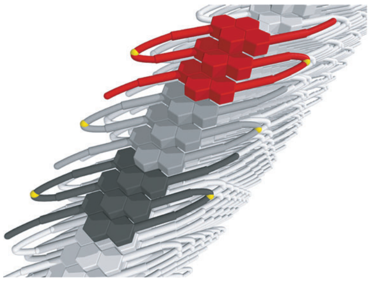
Essential utilities: The Li, Na, and K salts of 1,1,1,3,3,3-hexamethyldisilazide (HMDS, red), diisopropylamide (DA, green), and 2,2,6,6-tetramethylpiperidide (TMP, blue) constitute one of the most synthetically important classes of compounds. In this Review, these bulky secondary amides are considered collectively, and their effectiveness as reagents discussed on the basis of their solution behavior and solid-state structures.



For the USA and Canada: ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (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.

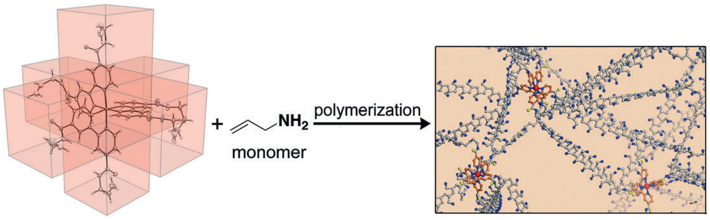
2D Supramolecular Polymers

Reading the bands: Amphiphilic pyrene trimers self-assemble into two-dimensional, supramolecular polymers in aqueous medium. Folding and aggregation processes are accompanied by simultaneous development of J- and H-bands and significant changes in the fluorescence properties. The formation of sheet-like nano-structures is confirmed by AFM.



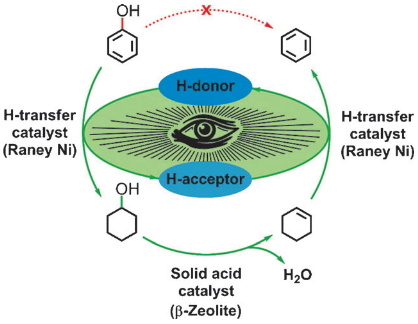
Frontispiece

Active Cross-Linkers



Chemomechanical reaction: The first octahedral ruthenium bipyridine complex that bears six polymerizable vinyl groups is used as an active cross-linker (see scheme, left). It is a key building block for cross-linked polymeric networks (right) thus allowing the construction of molecular architectures in chemomechanical soft materials.

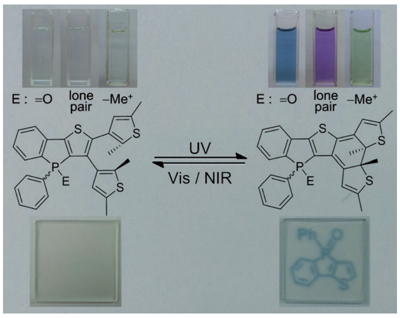
Heterogeneous Catalysis

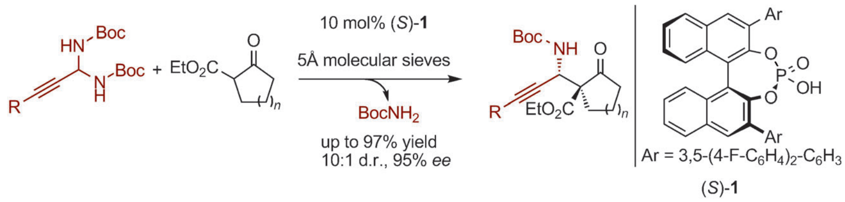


Finding a workaround: The conversion of lignin into low-boiling-point arenes instead of high-boiling-point phenols could greatly facilitate conventional refinery processes. A new procedure for the depolymerization of lignin and simultaneous conversion phenols into arenes is described. The method can also be rendered as a fundamental finding for the upgrade of bio-oils to arenes under mild conditions.

Photochromic Phospholes

Robust photoswitch: The photophysical and photochromic properties of a series of robust dithienylethene-containing phosphole derivatives can be readily tuned by simple modifications at the phosphorus center. Both the open and closed forms of the phosphole compounds are stable in benzene solution and in PMMA film in the dark.





Side by side: The title reaction is catalyzed by the chiral Brønsted acid (*S*)-**1**, and affords hitherto less accessible chiral propargylamines, having two adjacent stereocenters, in good to excellent diastereo- and enantioselectivities. Boc = *tert*-butoxycarbonyl.

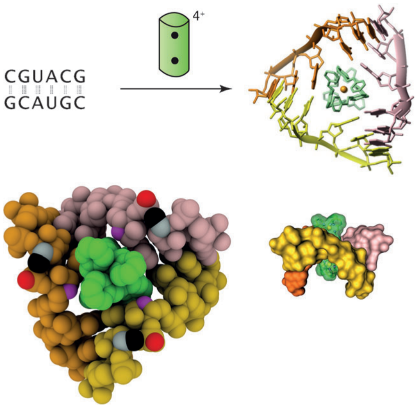
Asymmetric Catalysis

T. Kano, T. Yurino,
K. Maruoka* ———— **11509 – 11512**

Organocatalytic Asymmetric Synthesis of Propargylamines with Two Adjacent Stereocenters: Mannich-Type Reactions of In Situ Generated C-Alkynyl Imines with β-Keto Esters

---

Getting to the heart of it: Co-crystallization of an RNA three-way junction with a cylindrical di-iron(II)-based anti-cancer drug (green) results in π-stacking interactions between the cylinder and the central base pairs of the RNA structure. The shape, size, and cationic nature of the cylinder were found to be responsible for this perfect fit. Native gel electrophoresis studies confirmed stabilization of the RNA three-way junction by the iron(II) cylinder.

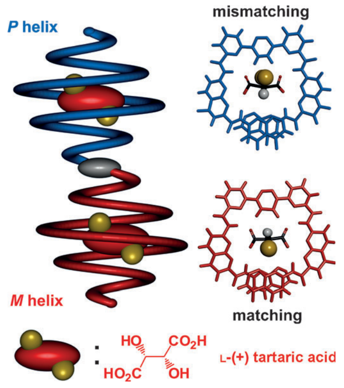


RNA Recognition

S. Phongtongpasuk, S. Paulus, J. Schnabl,
R. K. O. Sigel,* B. Spingler,*
M. J. Hannon,*
E. Freisinger* ———— **11513 – 11516**

Binding of a Designed Anti-Cancer Drug to the Central Cavity of an RNA Three-Way Junction

Front Cover



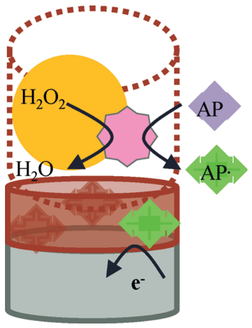
Racemic on the outside, but not inside: Aromatic-foldamer hosts are enantiomers and as such prefer to co-crystallize even though the guests (e.g. L-tartaric acid, see picture) in each host are not present as enantiomers. This behavior allows a one-step structure elucidation of diastereomeric and quasi-racemic structures in the solid state.

Quasiracemates

G. Lautrette, B. Kauffmann, Y. Ferrand,
C. Aube, N. Chandramouli, D. Dubreuil,
I. Huc* ———— **11517 – 11520**

Structure Elucidation of Host–Guest Complexes of Tartaric and Malic Acids by Quasi-Racemic Crystallography

---



Make it simple: A molecularly imprinted electropolymer was combined with an enzyme in a catalytic biomimetic sensor that enabled interference-free detection of the drug aminopyrine (AP) at submicromolar concentrations in the presence of ascorbic acid and uric acid within 15 s. The sensor functioned by the peroxide-dependent conversion of AP in a layer above a product-imprinted electropolymer on an indicator electrode (see picture).

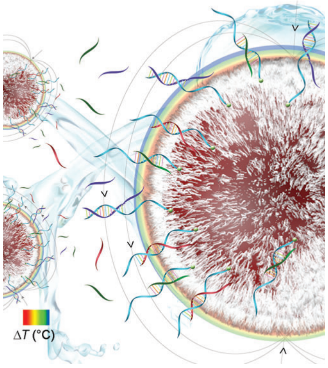
Biomimetic Sensors

A. Yarman,
F. W. Scheller* ———— **11521 – 11525**

Coupling Biocatalysis with Molecular Imprinting in a Biomimetic Sensor

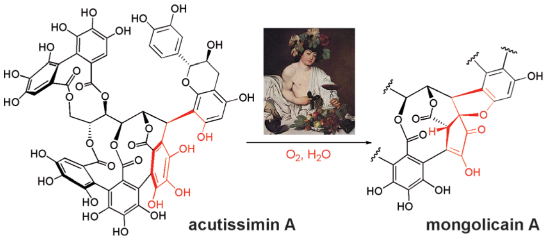
Molecular Temperature Probes

Inside Cover



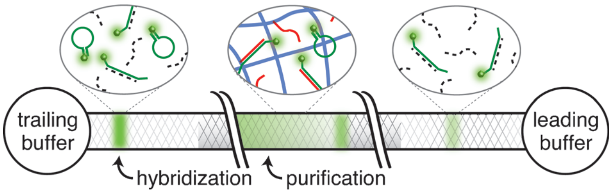
Too hot to handle: The surroundings of magnetic nanoparticles can be heated by applying a magnetic field. Polymer-coated magnetic nanoparticles were functionalized with single-stranded DNA molecules and further hybridized with DNA modified with different fluorophores. By correlating the denaturation profiles of the DNA with the local temperature, temperature gradients for the vicinity of the excited nanoparticles were determined.

Plant Polyphenols



Under the auspices of Bacchus! Acutissimins, natural flavano-ellagitannins, occur in oak-aged wine as a result of a diastereoselective condensation reaction of the flavan-3-ol catechin, a component of grapes, with the C-glucosidic ellagitannin vescalagin, found in oak. The acutissimins are further converted into natural mongolicains and analogues of camelliatannin G in a remarkably chemoselective fashion by simple aerobic oxidation.

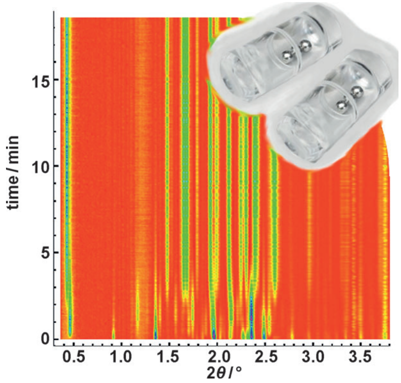
Analytical Methods



Focusing in on the small: A two-stage microRNA detection assay uses electrokinetic focusing to speed up hybridization and a functionalized hydrogel for affinity purification. This method detects microRNAs in 15 minutes with single-nucleotide specificity, and processes only 5 ng of total RNA.

Mechanisms of Mechanochemistry

Inside Back Cover

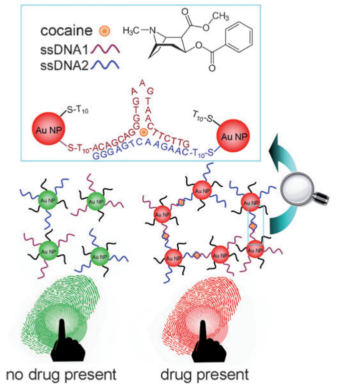


Looking in: The penetrating power of high-energy X-rays provides a means to monitor in situ and in real time the course of ball-milling reactions of organic pharmaceutical solids by detecting crystalline phases and assessing the evolution of their particle sizes. Upon switching from neat grinding to liquid-assisted grinding, cocrystal formation is enabled or tremendously accelerated, while the reaction mechanism alters its course.

Fingerprints

K. Li, W. W. Qin, F. Li, X. Zhao, B. Jiang, K. Wang, S. H. Deng, C. Fan,* D. Li* ———— **11542 – 11545**

Nanoplasmonic Imaging of Latent Fingerprints and Identification of Cocaine

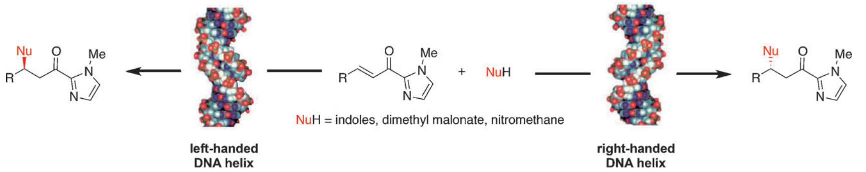


Search for traces: Aptamer-bound Au nanoparticles (Au NPs) were used to provide high-resolution dark-field microscopy images of latent fingerprints (LFPs) with level 2 and level 3 details. Furthermore, the cocaine-induced aggregation of Au NPs results in a true green-to-red color change of the scattered light, providing a quasi-quantative method to identify cocaine loadings in LFPs.

Asymmetric Catalysis

J. Wang, E. Benedetti, L. Bethge, S. Vonhoff, S. Klussmann, J.-J. Vasseur, J. Cossy, M. Smietana,* S. Arseniyadis* ———— **11546 – 11549**

DNA vs. Mirror-Image DNA: A Universal Approach to Tune the Absolute Configuration in DNA-Based Asymmetric Catalysis

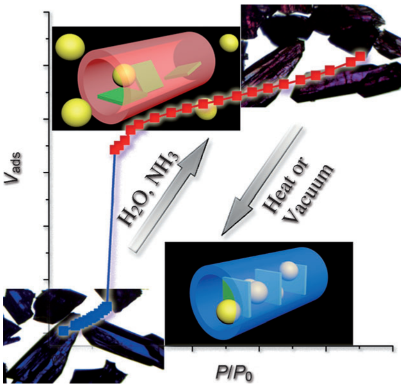


Mirror mirror on the wall: By taking advantage of the unique structural features of L-DNA, the first examples of left-helical enantioselective induction in the field of DNA-based asymmetric catalysis were realized. Most importantly, this approach is the only one that allows a reliable and predictable access to both enantiomers for any given reaction.

Dynamic Frameworks

Q. Chen, Z. Chang, W.-C. Song, H. Song, H.-B. Song, T.-L. Hu, X.-H. Bu* ———— **11550 – 11553**

A Controllable Gate Effect in Cobalt(II) Organic Frameworks by Reversible Structure Transformations

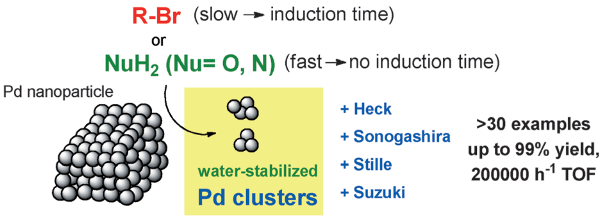


With H_2O or NH_3 stimuli, the blue cobalt-based metal–organic framework (MOF) BP can reversibly transform to red RP. The removal/recovery of terephthalate ligands accompanied by the transformation leads to a gate effect, which allows the encapsulation and release of small solvent molecules under certain conditions. This is the first example of topology transformation from a self-penetrating to interpenetrating net in 3D MOFs.

Palladium Catalysis

A. Leyva-Pérez, J. Oliver-Meseguer, P. Rubio-Marqués, A. Corma* ———— **11554 – 11559**

Water-Stabilized Three- and Four-Atom Palladium Clusters as Highly Active Catalytic Species in Ligand-Free C–C Cross-Coupling Reactions

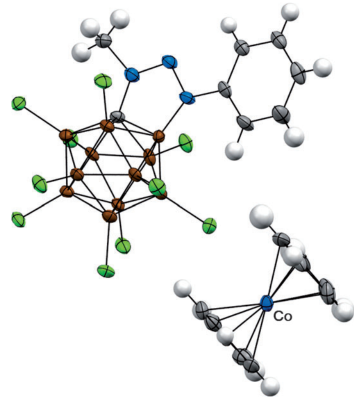


Elite cliques: Palladium clusters with three and four atoms were found to be the catalytically active species for ligand-free palladium-catalyzed C–C bond-forming reactions (see picture). These palladium cluster species could be stabilized in water and stored for long periods of time for use on demand with no loss of activity. High yields of products and turnover frequencies (TOFs) of up to 10^5 h^{-1} were observed.

Carborane Clusters

M. Asay, C. E. Kefalidis, J. Estrada, D. S. Weinberger, J. Wright, C. E. Moore, A. L. Rheingold, L. Maron,* V. Lavallo* ______ **11560 – 11563**

Isolation of a Carborane-Fused Triazole Radical Anion

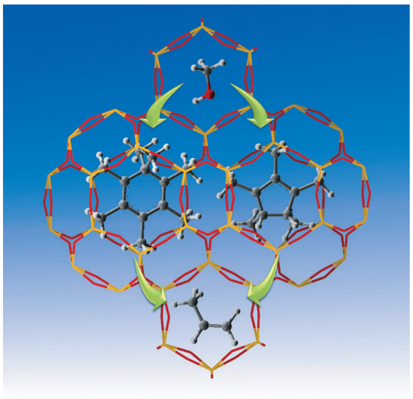


Outside the cage: A change in the redox properties of a triazole fused to a carborane anion through methylation to form a zwitterion enabled facile chemical reduction of the compound to an isolable triazole radical anion (see structure: C gray, H white, N blue, B brown, Cl green). The radical anion is stabilized by kinetic protection by the chlorinated carborane and the delocalization of spin density throughout the *exo*-cluster π system.

Reactive Intermediates

S. Xu, A. Zheng, Y. Wei, J. Chen, J. Li, Y. Chu, M. Zhang, Q. Wang, Y. Zhou, J. Wang, F. Deng, Z. Liu* **11564 – 11568**

Direct Observation of Cyclic Carbenium Ions and Their Role in the Catalytic Cycle of the Methanol-to-Olefin Reaction over Chabazite Zeolites



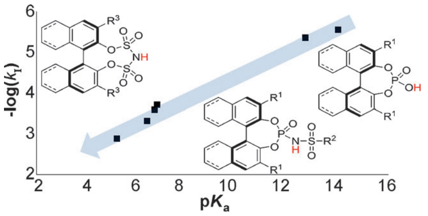
Carbenium ions in zeolites: Two important carbenium ions have been observed for the first time under working conditions of the methanol-to-olefins (MTO) reaction over chabazite zeolites using ^{13}C NMR spectroscopy. Their crucial roles in the MTO reaction cycles have been demonstrated by combining experiments and theoretical calculations.

Brønsted Acids

K. Kaupmees, N. Tolstoluzhsky, S. Raja, M. Rueping,* I. Leito* __ **11569 – 11572**

On the Acidity and Reactivity of Highly Effective Chiral Brønsted Acid Catalysts: Establishment of an Acidity Scale

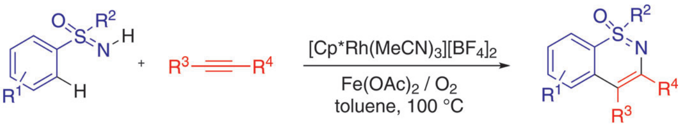
Stronger acid, higher speed: The pK_a values of a range of binol-derived Brønsted acids of three different types were measured and found to correlate directly with the catalytic properties of the acids: higher rate constants k_I were observed for more acidic Brønsted acid catalysts (see plot; binol = 1,1′-bi-2-naphthol).



C–H/N–H Activation

W. Dong, L. Wang, K. Parthasarathy, F. Pan, C. Bolm* ______ **11573 – 11576**

Rhodium-Catalyzed Oxidative Annulation of Sulfoximines and Alkynes as an Approach to 1,2-Benzothiazines

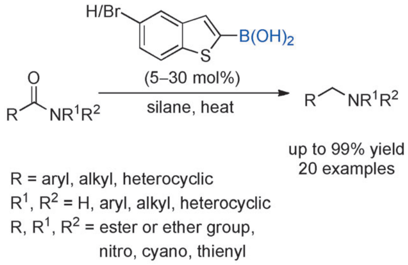


Revitalization by oxygen: A rhodium(III)-catalyzed oxidative C–H/N–H activation/annulation sequence provided access to a variety of substituted 1,2-benzothiazine derivatives from readily available *NH*-sulfoximines and alkynes (see scheme; Cp* = C_5Me_5). The oxidation system consisted of molecular oxygen in combination with a catalytic amount of Fe(OAc)$_2$.

Homogeneous Catalysis

Y. Li, J. A. Molina de La Torre, K. Grabow, U. Bentrup, K. Junge, S. Zhou, A. Brückner, M. Beller* —— 11577 – 11580

Selective Reduction of Amides to Amines by Boronic Acid Catalyzed Hydrosilylation

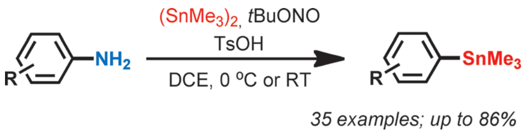


Not a 'B'ore! Benzothiophene-based boronic acids catalyze the reduction of tertiary, secondary, and primary amides in the presence of a hydrosilane. The reaction demonstrates good functional-group tolerance.

Synthetic Methods

D. Qiu, H. Meng, L. Jin, S. Wang, S. Tang, X. Wang, F. Mo, Y. Zhang,* J. Wang* —————— 11581 – 11584

Synthesis of Aryl Trimethylstannanes from Aryl Amines: A Sandmeyer-Type Stannylation Reaction

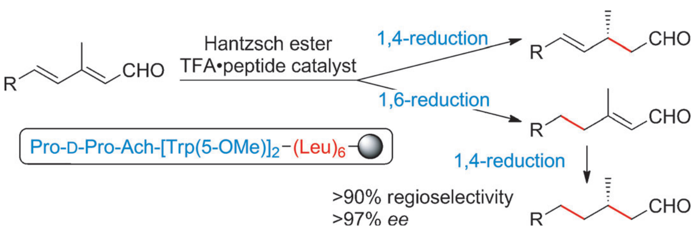


Sandmeyer-type stannylation: Stille coupling is one of the most powerful coupling reactions for C–C bond formation, whereas there are only limited methods to access aryl stannane compounds. A mild stannylation process based on a Sandmeyer-type transformation using aromatic amines as the starting materials is described. DCE: 1,2-dichloroethane.

Peptide Catalysis

K. Akagawa, J. Sen, K. Kudo* —————— 11585 – 11588

Peptide-Catalyzed Regio- and Enantioselective Reduction of α,β,γ,δ-Unsaturated Aldehydes

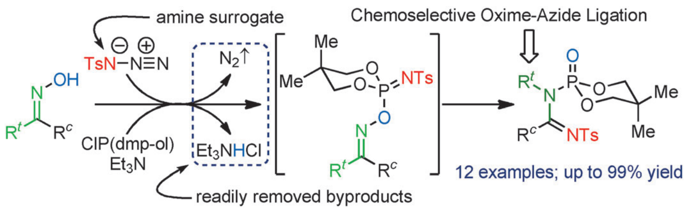


A resin-supported peptide catalyst (see box in the scheme) was used in the title reaction. The inherent regioselectivity was overcome by the peptide catalyst to promote the 1,6-selective reaction prior to 1,4-reduction. High stereoconvergence was also achieved when using a mixture of geometric isomers of the starting aldehydes. Ach = 1-amino-1-cyclohexanecarboxylic acid.

Synthetic Methods

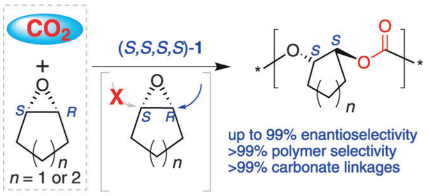
L. M. Fleury, E. E. Wilson, M. Vogt, T. J. Fan, A. G. Oliver, B. L. Ashfeld* ———— 11589 – 11593

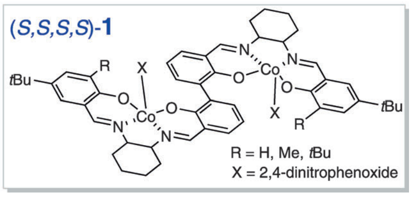
Amine-Free Approach toward *N*-Toluenesulfonyl Amidine Construction: A Phosphite-Mediated Beckmann-Like Coupling of Oximes and *p*-Toluenesulfonyl Azide



Atom hopping: A chlorophosphite-mediated Beckmann ligation of oximes and *p*-toluenesulfonyl azide gives access to *N*-sulfonyl phosphoramidines in good to excellent yields. The reaction proceeds under exceptionally mild conditions and constitutes a bioorthogonal approach toward amidines by avoiding the use of amines and transition-metal catalysts. dmp-ol = 3,3-dimethylpropanediol.

Polymerizations

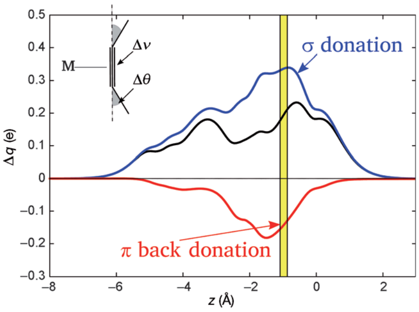




Unprecedented enantioselectivity and catalytic activity was observed in the asymmetric copolymerization of CO_2 with *meso*-epoxides (including the less reactive cyclopentene oxide) mediated by the dinuclear Co^{III} complex (*S*,*S*,*S*,*S*)-**1** under mild conditions. The resultant copolymers possess more than 99% carbonate linkages and a perfectly isotactic structure.

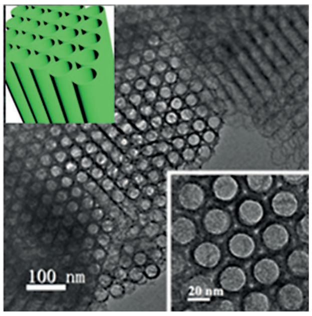
Bond Theory

A charge-displacement analysis of gold–ethyne complexes shows the existence of a quantitative relationship between measurable properties and the chemical bond constituents in the Dewar–Chatt–Duncanson model. Through suitable experiments, these constituents may be disentangled and crucial insight into the nature of coordination bonds may thus be gained.

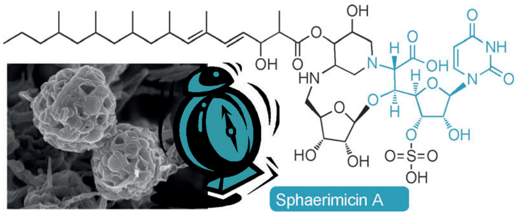


Mesoporous Materials

Ready to load: A shear stress regulated assembly route has been used to fabricate silica nanotubes and hollow mesostructures thereof. The packed silica nanotubes were employed as support for loading gold nanoparticles for efficiently catalyzing the epoxidation of styrene with high conversion and selectivity towards styrene oxide.



Natural Products

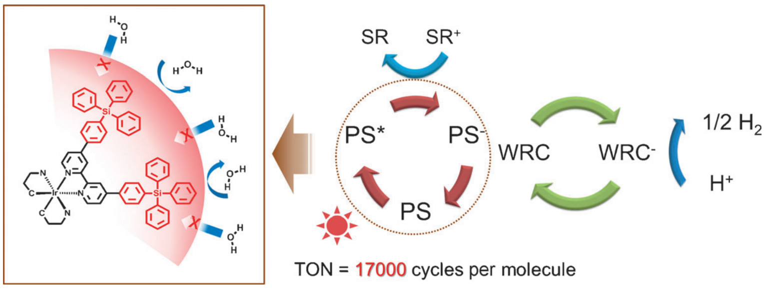


Rise and shine: Using a gene-targeting approach aimed at identifying potential L-threonine:uridine-5′-transaldolases that catalyze the formation of (5′*S*,6′*S*)-*C*-glycyluridine, a new bacterial translocase I inhibitor was discovered from an actinomycete following fermentation optimization.

Hydrogen Production

D. R. Whang, K. Sakai,
S. Y. Park* ———— 11612 – 11615

Highly Efficient Photocatalytic Water Reduction with Robust Iridium(III) Photosensitizers Containing Arylsilyl Substituents



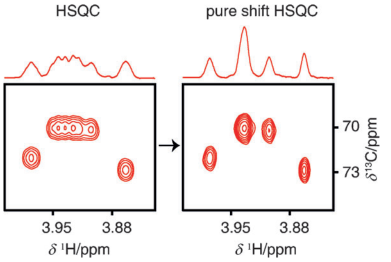
Waterproof complexes: Cationic Ir^{III} photosensitizers (PSs) with an ancillary 4,4′-bis(4-(triphenylsilyl)phenyl)-2,2′-bipyridine ligand enabled hydrogen evolution from water with high turnover numbers (TONs; see scheme). The peripheral triphenylsilyl moieties prevent ligand substitution by solvent molecules, such as water, and thus increase the durability of the complexes. SR = sacrificial reducing agent, WRC = water-reduction catalyst.

Pure Shift HSQC NMR

L. Paudel, R. W. Adams, P. Király,
J. A. Aguilar, M. Foroozandeh, M. J. Cliff,
M. Nilsson, P. Sándor, J. P. Waltho,
G. A. Morris* ———— 11616 – 11619

Simultaneously Enhancing Spectral Resolution and Sensitivity in Heteronuclear Correlation NMR Spectroscopy

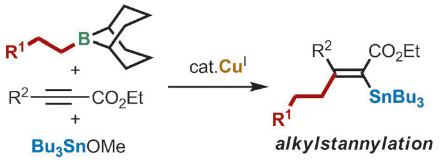
BIRD's eye view: Adding periodic BIRD J-refocusing (BIRD = bilinear rotation decoupling) to data acquisition in an HSQC experiment causes broadband homonuclear decoupling, giving a single signal for each proton chemical shift. This pure shift method improves both resolution and signal-to-noise ratio, without the need for special data processing.



Synthetic Methods

T. Wakamatsu, K. Nagao, H. Ohmiya,*
M. Sawamura* ———— 11620 – 11623

Synthesis of Trisubstituted Alkenylstannanes through Copper-Catalyzed Three-Component Coupling of Alkylboranes, Alkynoates, and Tributyltin Methoxide

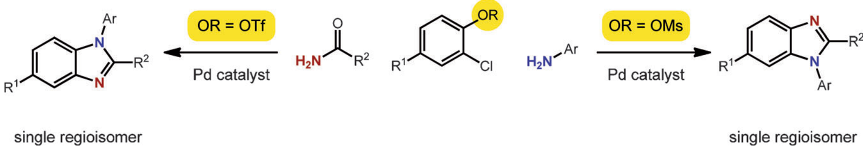


A versatile route to trisubstituted alkenylstannanes is presented. The alkyl and Sn moieties were introduced at the β and α carbon atoms of alkynoates, respectively, in a formal *syn* addition mode with complete regioselectivity (see scheme). A variety of functional groups were tolerated in the alkylboranes and alkynoates.

Homogeneous Catalysis

N. T. Jui, S. L. Buchwald* 11624 – 11627

Cascade Palladium Catalysis: A Predictable and Selectable Regiocontrolled Synthesis of *N*-Arylbenzimidazoles

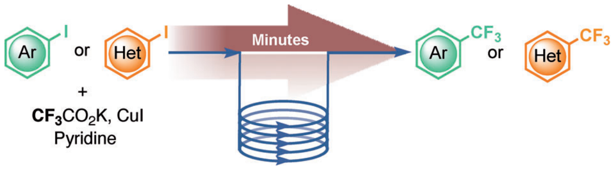


By choice: The palladium-catalyzed cascade reaction of 2-chloroaryl sulfonates with arylamine and amide nucleophiles provides direct access to *N*-arylbenzimidazoles. This strategy selectively produces the heterocycles based on chemoselective oxidative addition. 2-Chloroaryl triflates (Tf) produce one regioisomer and the corresponding 2-chloroaryl mesylates (Ms) deliver the other in a selectable manner.

Cross-Coupling

M. Chen, S. L. Buchwald* **11628 – 11631**

Rapid and Efficient Trifluoromethylation of Aromatic and Heteroaromatic Compounds Using Potassium Trifluoroacetate Enabled by a Flow System

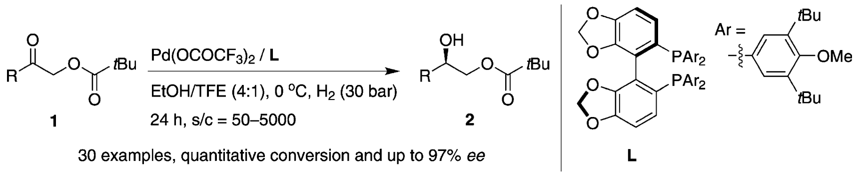


Going to the source: The trifluoromethylation of aryl/heteroaryl iodides has been demonstrated using a flow system, thus enabling a rapid rate of reaction. A broad spectrum of trifluoromethylated compounds was prepared in good to excellent yields using CF_3CO_2K as the trifluoromethyl source. The process has the advantage of short reaction times and uses convenient [CF_3] sources.

Homogeneous Catalysis

J. Chen, D. Liu, N. Butt, C. Li, D. Fan, Y. Liu, W. Zhang* **11632 – 11636**

Palladium-Catalyzed Asymmetric Hydrogenation of α-Acyloxy-1-arylethanones



First hand: The first example of a palladium-catalyzed asymmetric hydrogenation of α-acyloxy ketones (**1**) was accomplished to give the hydrogenated products **2** with by far the highest catalytic efficiency in up to quantitative conversions and excellent enantioselectivities. The hydrogenated products could serve as important intermediates for the preparation of many drug candidates. TFE = 2,2,2-trifluoroethanol.

DOI: 10.1002/anie.201308114

50 Years Ago ...

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

The next instalment of Rolf Huisgen's groudbreaking work on 1,3-dipolar cycloadditions was published in the form of a Review on their kinetics and mechanism. Studies on stereoselectivity, solvent and substituent effects, activation parameters, and orientation phenomena showed that the reaction proceeds by a concerted addition process.

Selenium chemistry was the subject of two contributions. In a Review, J. Gosselck discussed the chemistry of organoselenium compounds, including selenols, fluorinated organoselenium compounds, and selenium-containing carbenes. In a Communication, Max Schmidt et al. reported on the reactions of selenium trioxide, which reacts explosively with oxidizable compounds. Among the reactants investigated were thiols and hydrogen chloride.

Helmut Bredereck was the author of two papers in this issue. In a Review, the synthesis of substituted *s*-triazines from *N*-formyl compounds was discussed, and in a Communication, the reactions of *N*-alkylformamides with dimethyl sulfate were reported.

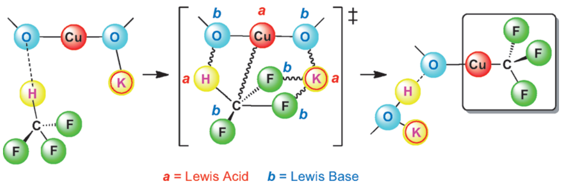
Directed aldol condensations to form α,β-unsaturated aldehydes were reported by Georg Wittig et al. Self-condensation of the aldehyde was avoided by metalating the corresponding Schiff base with lithium diethylamide, and the resulting organometallic species was found to add smoothly to ketones to give the target unsaturated aldehydes.

Read more in Issue 11/1963.

Fluoroform Activation

A. I. Konovalov, J. Benet-Buchholz,
E. Martin, V. V. Grushin* **11637 – 11641**

The Critical Effect of the Countercation in the Direct Cupration of Fluoroform with $[Cu(OR)_2]^-$

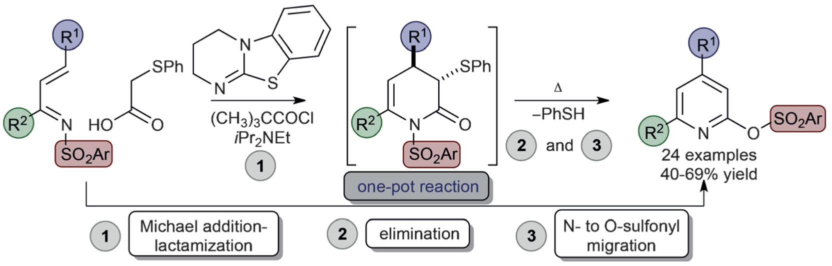


Just a spectator or a key player? The alkali-metal counterion (K^+) plays a remarkable key role in the recently discovered cupration reaction of fluoroform with dialkoxycuprates. A total of eight Lewis acid and Lewis base centers synergistically interacting with one another arrange in a stable transition state, providing a low-energy pathway for this unique transformation.

Heterocycles

D. G. Stark, L. C. Morrill, P.-P. Yeh,
A. M. Z. Slawin, T. J. C. O'Riordan,
A. D. Smith* **11642 – 11646**

Isothiourea-Mediated One-Pot Synthesis of Functionalized Pyridines



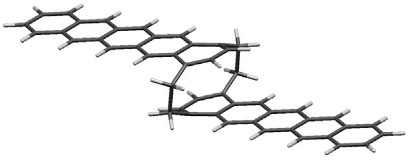
Acids to bases: The synthesis of 2,4,6-trisubstituted pyridines from (phenylthio)acetic acid and a range of α,β-unsaturated ketimines is reported. This process proceeds by intermolecular Michael addition/lactamization, thiophenol elimination, and N- to O-sulfonyl migration, giving 2-sulfonate-substituted pyridines which are readily derivatized to generate structural diversity.

Acenophanes

R. Bula, M. Fingerle, A. Ruff, B. Speiser,
C. Maichle-Mössmer,
H. F. Bettinger* **11647 – 11650**

Anti-[2.2](1,4)pentacenophane: A Covalently Coupled Pentacene Dimer

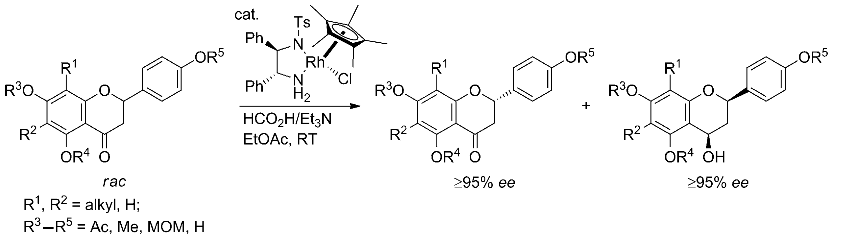
Two in a row: A pentacene dimer in which both units are covalently linked through a [2.2]paracyclophane bridge, has been synthesized (see picture). The electronic properties of the molecule were elucidated by a combination of experimental and computational methods. Such molecules could lead to materials with improved charge-transport properties.



Kinetic Resolution

M.-K. Lemke, P. Schwab, P. Fischer,
S. Tischer, M. Witt, L. Noehringer,
V. Rogachev, A. Jäger, O. Kataeva,
R. Fröhlich, P. Metz* **11651 – 11655**

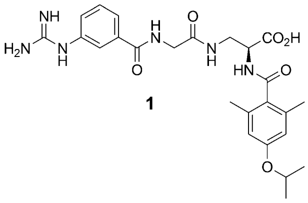
A Practical Access to Highly Enantiomerically Pure Flavanones by Catalytic Asymmetric Transfer Hydrogenation



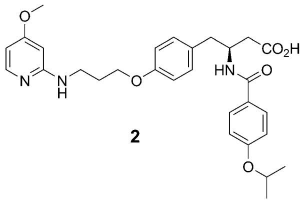
A surprisingly selective, non-enzymatic kinetic resolution of readily available, racemic β-chiral ketones enabled the title process, which was applied to a rapid synthesis of several bioactive flavanones in virtually enantiopure form (see scheme; MOM = methoxymethyl, Ts = *p*-toluenesulfonyl).

Integrins

Back Cover



1

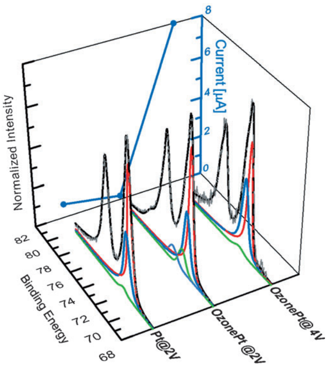


2

Pattern seekers: For the two angiogenic relevant integrins α5β1 and αvβ3, functionalized derivatives of the selective antagonists **1** and **2** could target and discriminate between tumor cells in vivo based on their different integrin patterns and also delay tumor growth in vivo. In addition, the first α5β1-selective integrin antagonist that enables specific molecular imaging by positron emission tomography was developed.

Oxygen Evolution

Chasing down the active state: Near-ambient-pressure X-ray photoelectron spectroscopy was used to study the surface of a Pt electrode during the oxygen evolution reaction (OER). A hydrated Pt metal phase with dissolved oxygen in the near-surface region is OER-active and considered to be the precursor of the analytically detected PtO_2, which is in fact the deactivation product of the electrode.



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

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

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.