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:*

*B. L. Merner, L. N. Dawe, G. J. Bodwell**
1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-walled Carbon Nanotube

*J. H. Ahn, B. Temel, E. Iglesia**
Selective Homologation Routes to 2,2,3-Trimethylbutane on Solid Acids

*B. Brugger, S. Rütten, K.-H. Phan, M. Möller, W. Richtering**
Colloidal Suprastructure of Smart Microgels at Oil/Water Interfaces

*B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia**
Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

*J. Tolosa, C. Kub, U. H. F. Bunz**
Hyperbranched: A Universal Conjugated Polymer Platform?

D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou,* K. Sun*
Solution-Based Evolution of Monodisperse Pt–Cu Nanocubes and Their Enhanced Methanol Oxidation Activity

*H. Moroder, J. Steger, D. Graber, K. Fauster, K. Trappl, V. Marquez, N. Polacek, D. N. Wilson, R. Micura**
Nonhydrolyzable RNA–Peptide Conjugates: A Powerful Advance in the Synthesis of Mimics for 3'-Peptidyl tRNA Termini

*J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich**
An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

*P. García-García, M. A. Fernández-Rodríguez, E. Aguilar**
Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

*H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen**
Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars and Polyhydroxylated α-Amino Acids

P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. J. Ragogna, C. L. B. Macdonald, K. M. Baines**
Cationic Crown Ether Complexes of Germanium(II)

News


J. Nørskov


M. Meldal


K. Ohmori

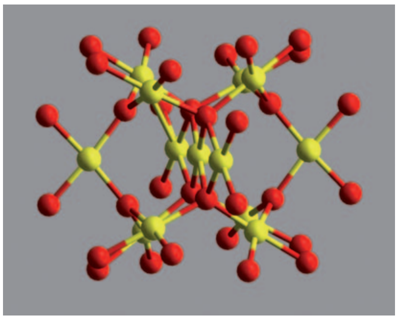
Author Profile

„The biggest challenge facing scientists is finding a way to make clean energy. If I could have dinner with three famous scientists from history, they would be Marie Curie, Dmitri Mendeleev, and Henri Moissan. ...“
This and more about Véronique Gouverneur can be found on page 3559.

Books

Highlights

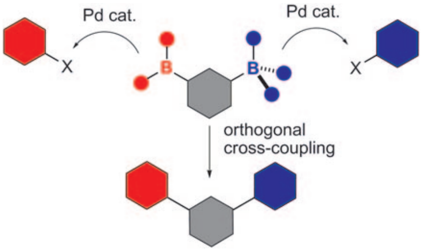
Polyoxometalates



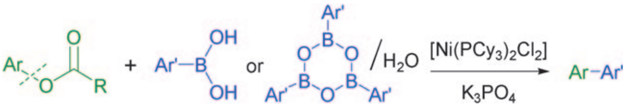
A good model? Noble-metal particulate catalysts often require small amounts of oxygen to obtain optimal activity. However, the structure and stoichiometry of the oxidized metal clusters involved remains obscure, even almost two hundred years after their discovery. A heteropolypalladate salt (see picture; Pd yellow, O red) now offers a view of how oxygen might be incorporated into small noble-metal clusters.

Cross-Coupling

Seeing the sites: The Suzuki–Miyaura reaction of substrates containing multiple coupling sites has been performed in a directed manner through the reactivity modulation of the boron moiety (see scheme). Several other strategies are also discussed.



C–O Activation



Crucial breakthroughs in the activation of the C(aryl)–O bond of phenol derivatives were achieved almost simultaneously by two research groups (see scheme; Cy = cyclohexyl). Garg et al. coupled a range of aryl pivalates with arylboronic acids to give unsymmetrical biaryls. Shi et al. achieved this through C(aryl)–O activation of aryl carboxylates; the best results for the coupling of aryl boroxines were again obtained with aryl pivalates.

For the USA and Canada:
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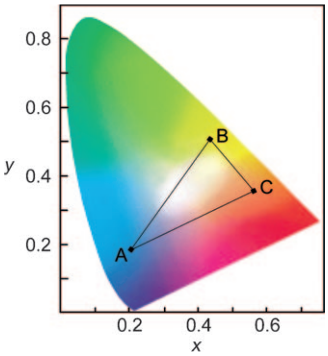
Minireviews

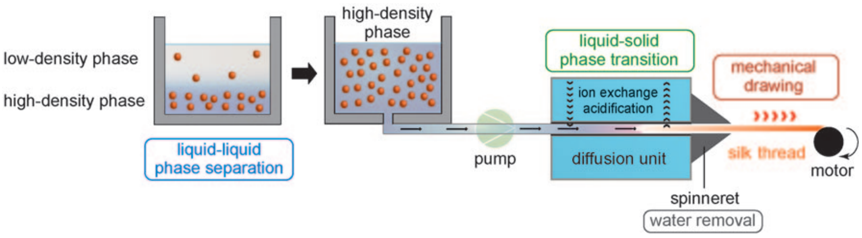
Luminescent Materials

Energy efficiency is in! New inorganic luminescent materials can help to increase energy efficiency when used in plasma display panels and white-light-emitting diodes (see color diagram; mixing the three emissions A–C produces any given point within the triangle). In mercury-free fluorescent lamps these phosphors might contribute to environmental protection, and they provide better scintillation materials for medical diagnostics.



Reviews

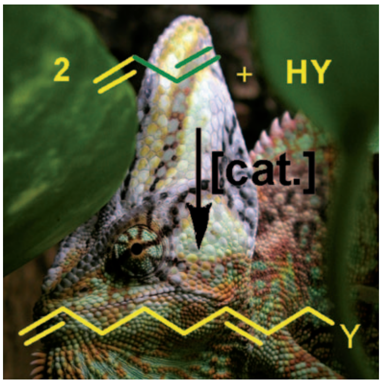
Biomimetic Polymers



On a silky thread: Spider silks have mechanical properties that outperform most natural and synthetic fibers. Classical spinning methods have failed to mimic the highly complex natural in-vivo spinning process. Analyzing this process in combination with in-vitro findings allows the development of biomimetic spinning devices for the technical production of silk fibers (see picture).

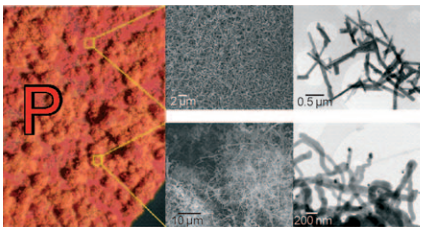
Telomerization

A chameleonic reaction: The transition-metal-catalyzed telomerization of 1,3-dienes with different nucleophiles leads to the synthesis of numerous products which can be applied in the cosmetic and pharmaceutical industry as well as in polymers and flavors. This Review shows the versatility of the telomerization based on recent research and industrial applications.

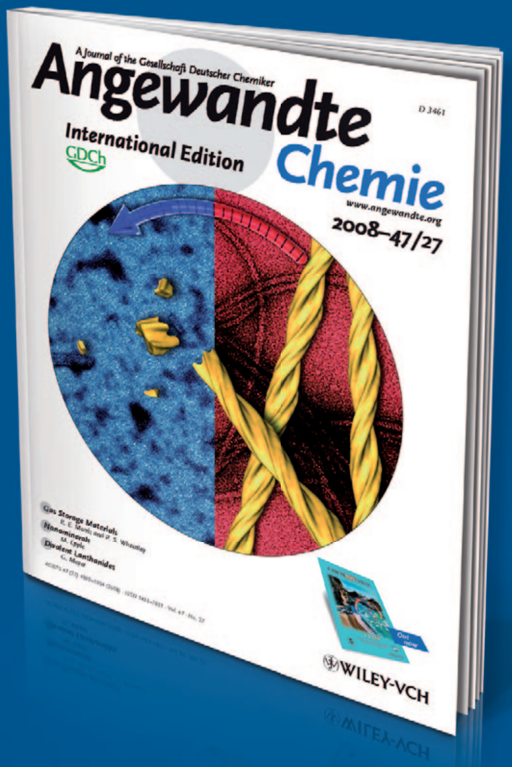


Communications

Phosphorus Nanostructures



To Bi or not to Bi? The synthesis of phosphorus nanorods of two differing morphologies is reported, in both the presence and absence of a bismuth catalyst. Not only do these materials represent a new class of elemental nanorods but they also give valuable insight into the complex allotropy of phosphorus.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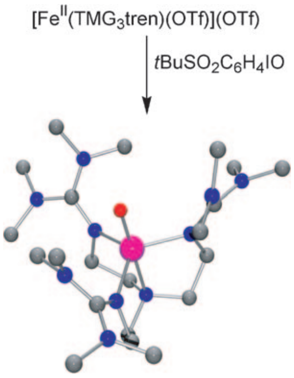
Nonheme Iron Complexes

J. England, M. Martinho, E. R. Farquhar, J. R. Frisch, E. L. Bominaar,* E. Münck,* L. Que, Jr.* ________ **3622 – 3626**

A Synthetic High-Spin Oxoiron(IV) Complex: Generation, Spectroscopic Characterization, and Reactivity

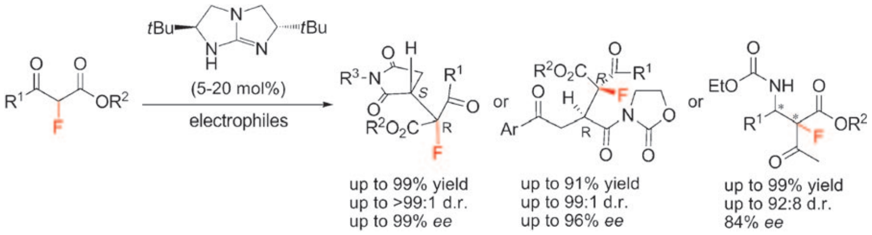


High versus low: The high-yield generation of a synthetic high-spin oxoiron(IV) complex, $[Fe^{IV}(O)(TMG_3tren)]^{2+}$ (see picture, TMG_3tren = 1,1,1-tris{2-[N2-(1,1,3,3-tetramethylguanidino)]ethyl}-amine), has been achieved by using the very bulky tetradentate TMG_3tren ligand, in order to both sterically protect the oxoiron(IV) moiety and enforce a trigonal bipyramidal geometry at the iron center, for which an $S = 2$ ground state is favored.

Asymmetric Synthesis

Z. Jiang, Y. Pan, Y. Zhao, T. Ma, R. Lee, Y. Yang K.-W. Huang, M. W. Wong,* C.-H. Tan* ________ **3627 – 3631**

Synthesis of a Chiral Quaternary Carbon Center Bearing a Fluorine Atom: Enantio- and Diastereoselective Guanidine-Catalyzed Addition of Fluorocarbon Nucleophiles

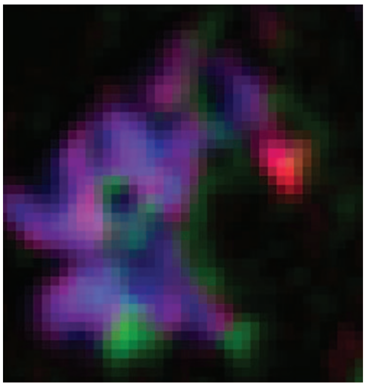


The perfect combination: The title reaction provides adducts having quaternary carbon centers bearing a fluorine atom with high *ee* and d.r. values (see scheme). The mechanism and origin of stereoselectivity were elucidated by DFT calculations. The bifunctional mode of the guanidine catalysis was demonstrated in the transition states resulting from the DFT results.

Heterogeneous Catalysis

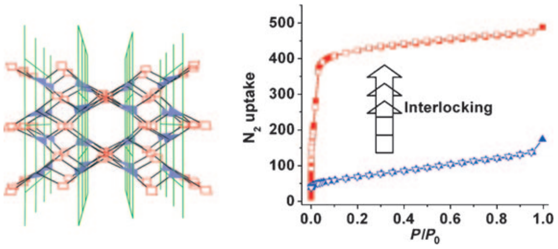
E. de Smit, I. Swart, J. F. Creemer, C. Karunakaran, D. Bertwistle, H. W. Zandbergen, F. M. F. de Groot,* B. M. Weckhuysen* ________ **3632 – 3636**

Nanoscale Chemical Imaging of the Reduction Behavior of a Single Catalyst Particle



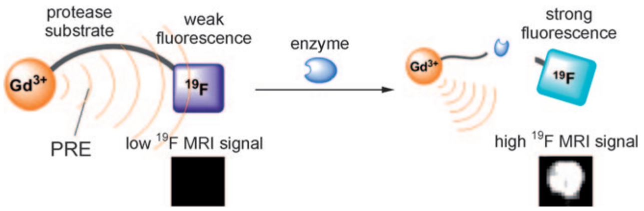
A closer look: Investigation of the reduction properties of a single Fischer–Tropsch catalyst particle, using in situ scanning transmission X-ray microscopy with spatial resolution of 35 nm, reveals a heterogeneous distribution of Fe^0, Fe^{2+}, and Fe^{3+} species. Regions of different reduction properties are defined and explained on the basis of local chemical interactions and catalyst morphology.

Metal–Organic Frameworks



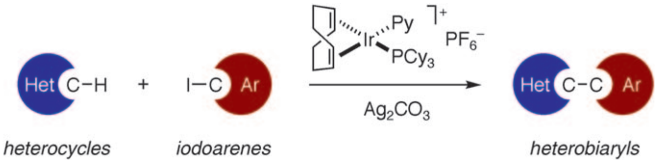
Stop the breathing: As the organic bridging ligands become more elaborate and large, the resulting MOFs tend to experience significant framework distortion (i.e., breathing) upon solvent removal. Rigidification of MOFs that are built from elongated tetracarboxylate bridging ligands by unusual interlocking and interpenetration leads to highly porous and robust hybrid materials.

Molecular Imaging



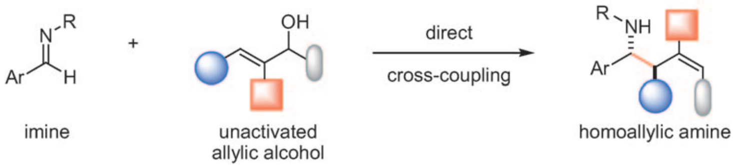
Dynamic duo: Magnetic resonance imaging (MRI) can visualize deep regions of living bodies, whereas fluorescence measurement offers excellent sensitivity. These methods thus offer signal enhancement potential for detecting enzyme activities. A dual-mode off/on probe to detect caspase-3 activity by fluorescence and ^{19}F MRI is presented.

Synthetic Methods



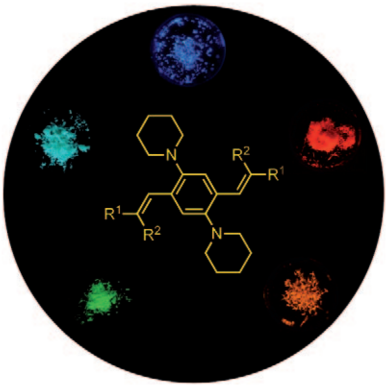
Efficient couplings using equimolar quantities of each coupling partner and multiple C–H bond arylation reactions are achieved with an Ir-based catalytic system for the C–H bond arylation of electron-rich heteroarenes with iodoarenes to construct extended π-systems. The dramatic ligand effect on reaction efficiency leads to the discovery that Crabtree's catalyst (see scheme) is the optimal catalyst precursor.

Synthetic Methods



Regioselective, stereoselective: The convergent coupling of allylic alcohols with imines to deliver stereodefined homoallylic amines is described (see scheme). The process proceeds with net allylic transposition without the intermediacy of allylic organometallic reagents. Two stereodefined centers and a geometrically defined di- or trisubstituted alkene are forged with high selectivity.

Minimum requirements: Crystals and thin films of 1,4-bis(alkenyl)-2,5-dipiperidinobenzenes, which contain only one benzene ring as the aromatic component, emit visible light with excellent solid-state quantum yields upon irradiation with UV light. Polystyrene thin films doped with the benzenes also exhibit brilliant fluorescence. By modifying the alkenyl groups, the emission color can be tuned in the range from blue to red.



Fluorescent Materials

M. Shimizu,* Y. Takeda, M. Higashi, T. Hiyama ———— **3653 – 3656**

1,4-Bis(alkenyl)-2,5-dipiperidinobenzenes: Minimal Fluorophores Exhibiting Highly Efficient Emission in the Solid State

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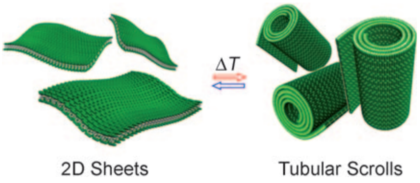
Deep-water scrolls: It is demonstrated that amphiphilic rods containing lateral flexible chains self-assemble into two-dimensional sheets in aqueous solution (see picture). Remarkably, the sheets roll up reversibly into tubular scrolls upon heating, as confirmed by cryo-transmission electron microscopy and fluorescence microscopy.



Nanotubes

E. Lee, J.-K. Kim, M. Lee* ———— **3657 – 3660**

Reversible Scrolling of Two-Dimensional Sheets from the Self-Assembly of Laterally Grafted Amphiphilic Rods

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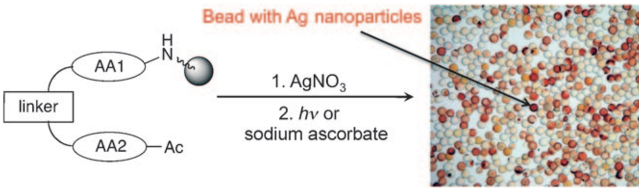

Split-and-mix libraries are an excellent tool for the identification of peptides that induce the formation of Ag nanoparticles in the presence of either light or sodium ascorbate to reduce Ag^+ ions. Structurally diverse peptides were detected in colorimetric on-bead screenings that generate Ag nanoparticles of different sizes, as confirmed by SEM and X-ray powder diffraction studies.

Nanostructures

K. Belser, T. Vig Slenters, C. Pfumbidzai, G. Upert, L. Mirolo, K. M. Fromm,* H. Wennemers* ———— **3661 – 3664**

Silver Nanoparticle Formation in Different Sizes Induced by Peptides Identified within Split-and-Mix Libraries

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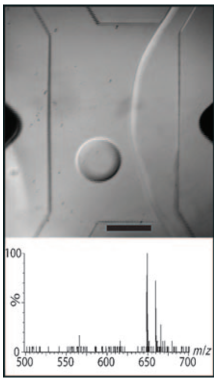
Fully integrated: Mass spectrometry has been integrated into a detection scheme for microdroplets that are created within microfluidic channels (see picture, scale bar 200 μm). This technique allows droplets to be identified based on the compounds they contain, and combines fluorescence screening with MS analysis. These experiments indicate how similar approaches can be applied to the ambitious goals of on-chip protein evolution and chemical synthesis.



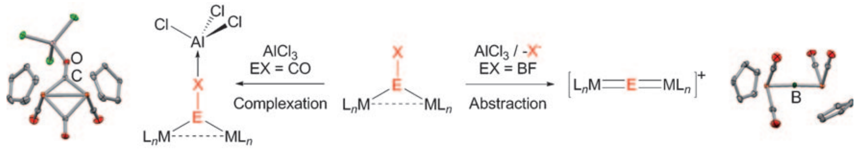
Microdroplets

L. M. Fidalgo, G. Whyte, B. T. Ruotolo, J. L. P. Benesch, F. Stengel, C. Abell, C. V. Robinson, W. T. S. Huck* ———— **3665 – 3668**

Coupling Microdroplet Microreactors with Mass Spectrometry: Reading the Contents of Single Droplets Online

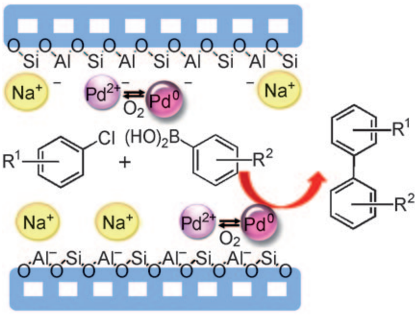
Contents

CO Analogues



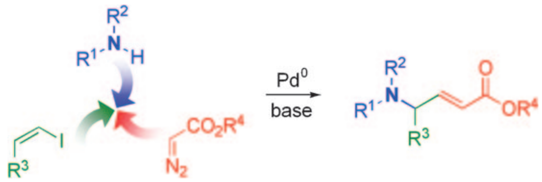
No CO: Fluoroborylene (BF), isoelectronic with CO and N_2, can be trapped by a transition metal. The structurally characterized complex $[\{CpRu(CO)_2\}_2(\mu\text{-}BF)]$ contains an unsupported bridging BF ligand, which is unprecedented in the structural chemistry of CO. With $AlCl_3$, metal-bound CO coordinates through the O atom without bond rupture, while the more polar and less π-bonded BF ligand is heterolytically cleaved (see picture).

Heterogeneous Catalysis



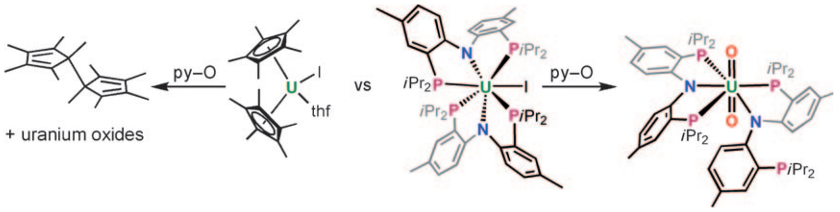
Exchange for the better: Mesoporous sodalite and NaA zeolite exchanged with Pd^{2+} exhibit remarkably high activity and reusability in C–C coupling reactions under aerobic atmosphere. It is proposed that the catalytic reactions are mediated by a molecular Pd^0 species generated in situ within the pores (see picture), which is oxidized back to Pd^{2+} by O_2, preventing the formation of catalytically inactive Pd^0 agglomerates.

Synthetic Methods



As easy as 1, 2, 3: A palladium-catalyzed three-component coupling generates α,β-unsaturated γ-amino acids in a single step (see scheme). The reaction is believed to involve migration of a vinyl substituent to a highly electrophilic palladium carbene. Unlike previous synthetic approaches, this synthesis provides access to γ-amino acids with non-natural side chains.

Actinide Chemistry

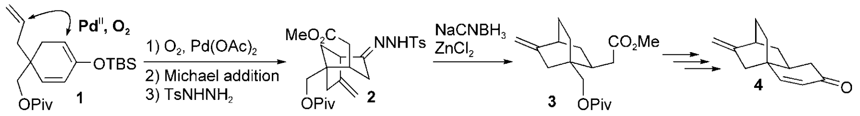


A soft embrace for U: Replacement of C_5Me_5 by the soft PNP pincer ligand is a successful strategy to promote new reactivities and support new structures for the actinide series (see picture, py–O = pyridine-*N*-oxide). The specific electronic and steric properties of the PNP ligand enable access to previously unreported structures not available for the C_5Me_5 ligand set and support not only low-valent uranium but also the high-valent uranium(VI) ion.

Natural Products Synthesis

G. N. Varseev, M. E. Maier* **3685 – 3688**

Formal Total Synthesis of Platencin



The right bicycle: A concise formal synthesis of platencin was based on an efficient oxygen-mediated palladium-catalyzed cycloalkenylation of **1** to form a bicyclo[3.2.1]octane, and a deoxygenative rearrangement of tosylhydrazone **2** to construct the bicyclo[2.2.2]octane **3**. The total yield of the core structure **4** of platencin was 17.5 % for 13 steps from a commercially available compound. Ts = *p*-toluenesulfonyl, TBS = *tert*-butyldimethylsilyl, Piv = pivaloyl.

Multicomponent Reactions

S. N. Greszler,
J. S. Johnson* ——— **3689 – 3691**

Diastereoselective Synthesis of Pentasubstituted γ-Butyrolactones from Silyl Glyoxylates and Ketones through a Double Reformatsky Reaction

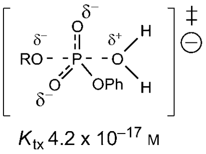
Three contiguous stereocenters can be established with remarkable diastereoselectivity in a double Reformatsky sequence. Densely functionalized γ-butyrolactones were assembled rapidly by this approach, in which a ketone is used as the terminal electrophile (see scheme). Secondary transformations of the lactone products enhance their synthetic utility. R^1 = Me, H; R^2 = alkyl, aryl, CF_3; Bn = benzyl, TBS = *tert*-butyldimethylsilyl.

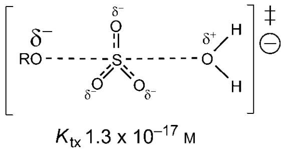
Catalytic Promiscuity

A. C. Babtie, S. Bandyopadhyay,
L. F. Olguin, F. Hollfelder* **3692 – 3694**

Efficient Catalytic Promiscuity for Chemically Distinct Reactions

High catalytic proficiencies observed for the native and promiscuous reaction of the *Pseudomonas aeruginosa* arylsulfatase (PAS; the picture shows transition states of the two substrates with corresponding binding constants K_{tx}) suggest that the trade-off between high activity and tight specificity can be substantially relaxed.

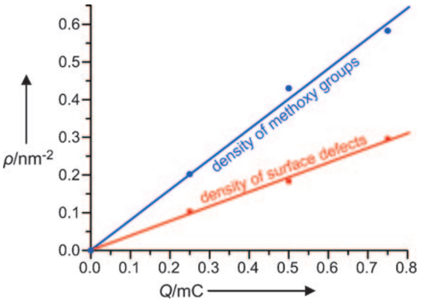




Surface Chemistry

D. Göbke, Y. Romanyshyn, S. Guimond,
J. M. Sturm, H. Kuhlenbeck,* J. Döbler,
U. Reinhardt, M. V. Ganduglia-Pirovano,
J. Sauer, H.-J. Freund ——— **3695 – 3698**

Formaldehyde Formation on Vanadium Oxide Surfaces V_2O_3(0001) and V_2O_5(001): How does the Stable Methoxy Intermediate Form?

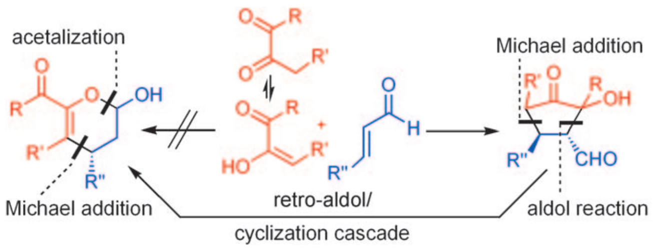


Hydroxy-mediated methoxy formation or stabilization is probably an important process in many methanol adsorption systems. Hydrogen atoms originating from the scission of the methanol O–H bond react with the substrate and form water. This process may result 1) in the production of additional surface defects as reactive centers for methoxy formation and 2) in the stabilization of methoxy groups by suppression of methanol formation.

Asymmetric Domino Catalysis

M. Rueping,* A. Kuenkel, F. Tato,
J. W. Bats ——— **3699–3702**

Asymmetric Organocatalytic Domino Michael/Aldol Reactions: Enantioselective Synthesis of Chiral Cycloheptanones, Tetrahydrochromenones, and Polyfunctionalized Bicyclo[3.2.1]octanes



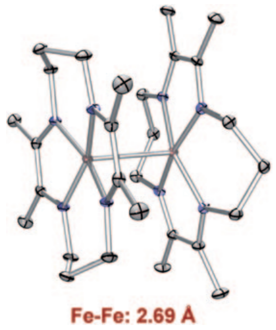
C′mon 1,2-dione: A new diastereo- and enantioselective Lewis base catalyzed domino Michael/aldol reaction converts α,β-unsaturated aldehydes and 1,2-diones into chiral bicyclo[3.2.1]octane-6-carbaldehydes. The products are produced in good to excellent enantioselectivities (90–98% *ee*) and can be transformed into bicyclic diols and triols. Additionally, a retro-aldol cyclization provides access to valuable tetrahydrochromenones (see scheme).

Fe–Fe Dimer with Redox-Active Ligands

C. R. Hess, T. Weyhermüller, E. Bill,
K. Wieghardt* ——— **3703–3706**

[{Fe(tim)}$_2$]: An Fe–Fe Dimer Containing an Unsupported Metal–Metal Bond and Redox-Active N$_4$ Macrocyclic Ligands

Mixed doubles: The dimeric complex [{Fe(tim)}$_2$] (see structure, tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) represents an unprecedented complex containing an unsupported Fe–Fe bond. The crystal structure confirms the presence of reduced tim units, thus indicating ligand redox activity. Spectroscopic and computational studies establish a triplet ground state for [{Fe(tim)}$_2$] and suggest a mixed-valence compound with respect to both the Fe ions and the ligands.



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).

Service

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