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:

*Q. Wang, M. Zhang, C. Chen, W. Ma, J. Zhao**
Photocatalytic Aerobic Oxidation of Alcohols on TiO_2: The Acceleration Effect of Brønsted Acids

Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan, C. He**
AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA

*S. Rizzato, J. Bergès, S. A. Mason, A. Albinati, J. Kozelka**
Dispersion-Driven Hydrogen Bonding: Theoretically Predicted H–bond between H_2O and Platinum(II) Identified by Neutron Diffraction

H. Amouri, J. Moussa, A. K. Renfrew, P. J. Dyson, M. N. Rager, L.-M. Chamoreau*
Metal Complex of Diselenobenzoquinone: Discovery, Structure, and Anticancer Activity

M. R. Leone, G. Lackner, A. Silipo, R. Lanzetta, A. Molinaro, C. Hertweck**
An Unusual Galactofuranose Lipopolysaccharide Warrants Intracellular Survival of Toxin–Producing Bacteria in their Fungal Host

M. Roth, P. Kindervater, H.-P. Raich, J. Bargon, H. W. Spiess, K. Münnemann**
Continuous ^1H and ^{13}C Signal Enhancement in NMR and MRI Using Parahydrogen and Hollow-Fiber Membranes

*H. Zheng, J. Gao**
Highly Specific Heterodimerization Mediated by Quadrupole Interactions

*H. Shao, J. Seifert, N. C. Romano, M. Gao, J. J. Helmus, C. P. Jaroniec, D. A. Modarelli, J. R. Parquette**
Amphiphilic Self-Assembly of an *n*–Type Nanotube

Author Profile

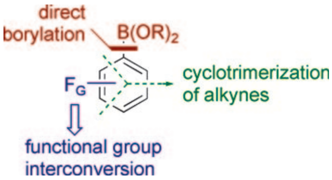
"My favorite subject at school was music.
The biggest challenge facing scientists is … to understand the function of the brain. …"
This and more about Otto S. Wolfbeis can be found on page 7160.

Books

Highlights

Arylboronates

Form and function: Cross-coupling reactions are fundamental processes for C–C bond formation in arene chemistry. But the utility of those reactions is determined by the availability of a suitable number of adequately functionalized substrates. This Highlight discusses the preparation of functionalized arylboronates of synthetic utility (see scheme; F_G = functional group).

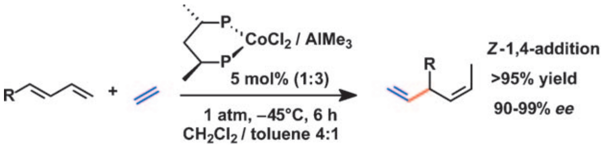


Contents

Asymmetric Catalysis

D. Vogt* ________ **7166 – 7168**

Cobalt-Catalyzed Asymmetric Hydrovinylation



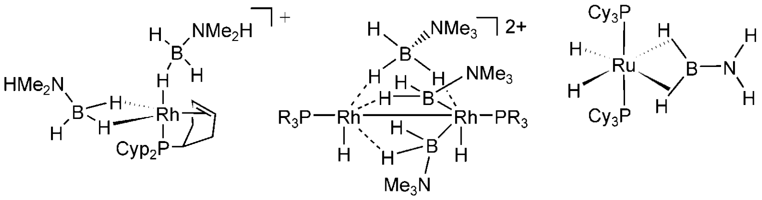
Back to the first row: A surprisingly simple protocol involving chiral diphosphine complexes of cobalt(II) salts allows the highly enantioselective hydrovinylation of 1,3-dienes in extremely high selectivities and yields.

Minireviews

Coordinated Amine–Boranes

G. Alcaraz,*
S. Sabo-Etienne* ________ **7170 – 7179**

Coordination and Dehydrogenation of Amine–Boranes at Metal Centers



Debaser: Key elementary steps in the activation of $H_3B{-}NH_3$ and derivatives upon coordination to a metal fragment have been identified. Recent results in the metal-induced dehydrogenation of amine–boranes show the importance of the B–H bond-activation step. Isolated complexes show unprecedented amine–borane bonding modes and H_2BNH_2 trapping on a metal center thanks to a bis(σ-B–H) mode.

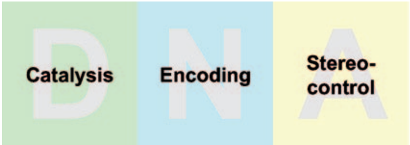
Reviews

Applications of DNA

S. K. Silverman* ________ **7180 – 7201**

DNA as a Versatile Chemical Component for Catalysis, Encoding, and Stereocontrol

Beyond biological DNA: Chemists are exploiting DNA for interesting applications as a catalyst, encoding component, and stereocontrol element. Each of these chemical applications takes advantage of a distinct subset of DNA’s properties in ways not known in nature.



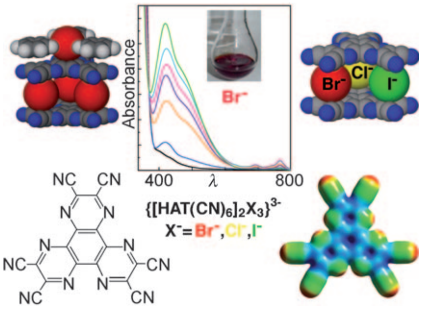
Communications

Anion Interactions

H. T. Chifotides,* B. L. Schottel,
K. R. Dunbar* ________ **7202 – 7207**

The π-Accepting Arene HAT(CN)$_6$ as a Halide Receptor through Charge Transfer: Multisite Anion Interactions and Self-Assembly in Solution and the Solid State

Sensitive molecular scaffold: The exceptional π-electron-acceptor strength of HAT(CN)$_6$ renders it an excellent colorimetric halide sensor. It engages in multisite anion interactions, namely, both charge-transfer and anion–π, in solution and the solid state. The halide ions are the driving elements for the spontaneous self-assembly of the sandwich-like complexes through η^2,η^2-charge-transfer contacts.



For the USA and Canada:
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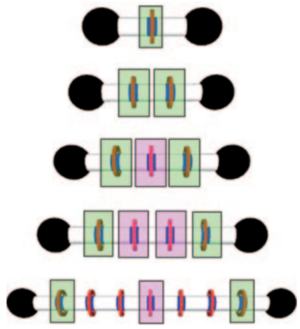
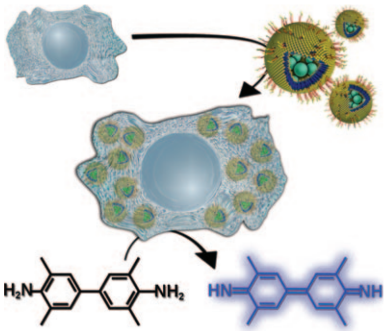
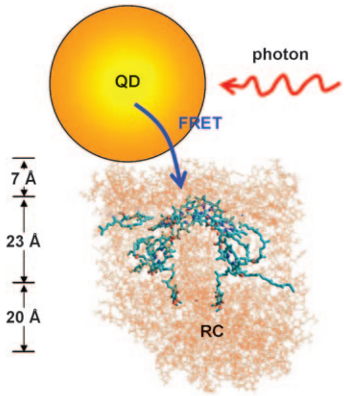


Strategically placing secondary dialkylammonium recognition sites at the magic distance of 3.5 Å apart in the dumbbell components of a series of oligorotaxanes (see picture) renders otherwise conformationally floppy [*n*]rotaxanes rigid and rodlike. These oligorotaxanes form with near-quantitative conversion under thermodynamic control using dynamic covalent chemistry.

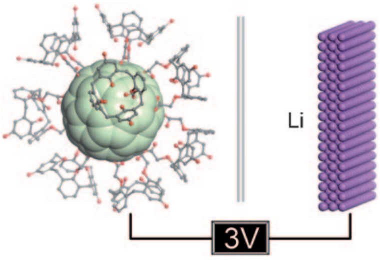
Cells with implants: Porous enzyme-loaded polymersomes were constructed that display the cell-penetrating peptide tat on their surfaces. These nanoreactors are taken up by mammalian cells through macropinocytosis. Inside the cells, the polymersomes are only partially routed to acidic compartments. Polymersomes with horseradish peroxidase as a model cargo enzyme displayed sustained intracellular activity.



Bio–nano: Quantum dots (QDs) can be tagged with photosynthetic reaction centers (RCs) in such a way (see picture) that FRET from the QD to the RC leads to a near-threefold increase in the rate of generation of excitons in the RC over that in the RC alone. Even-stronger enhancements are predicted, thus indicating that such complexes may significantly improve the efficiency of photosynthesis.



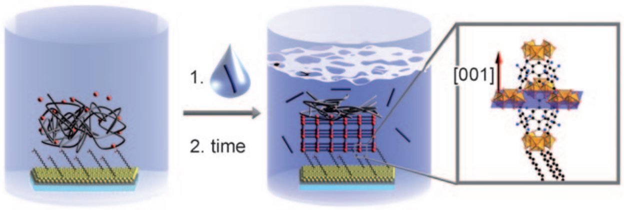
Active monomers: Grafting soluble organic molecules onto insoluble, high-surface-area substrates, e.g. calixquinones on nanoparticles (see pciture), allows the production of a wide range of very stable materials for lithium-ion battery applications. Immobilization of the organic molecules avoids the problem of dissolution, which has previously led to performance degradation.



Metal–Organic Frameworks

A. Schoedel, C. Scherb,
T. Bein* ________________ 7225 – 7228

Oriented Nanoscale Films of Metal–Organic Frameworks By Room-Temperature Gel-Layer Synthesis

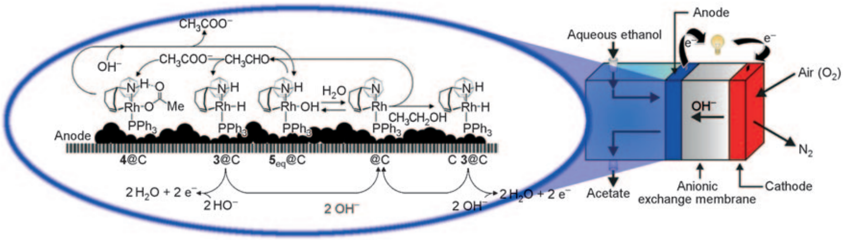


MOF Brylcreem: A gel-layer-based strategy is used for the growth of highly oriented thin films of metal–organic frameworks on self-assembled monolayers attached to a gold slide. The monolayer is loaded with the metal-salt-containing poly(ethylene glycol) gel layer (see picture; metal ions in red) and covered with a solution containing the linker molecules (blue).

Organometallic Fuel Cells

S. P. Annen, V. Bambagioni,
M. Bevilacqua, J. Filippi, A. Marchionni,
W. Oberhauser, H. Schönberg,
F. Vizza,* C. Bianchini,*
H. Grützmacher* __________ 7229 – 7233

A Biologically Inspired Organometallic Fuel Cell (OMFC) That Converts Renewable Alcohols into Energy and Chemicals

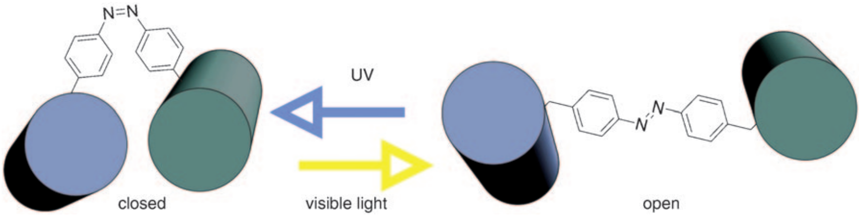


Embedded and working: The intact deposition of a complex into carbon powder allows the construction of an organometallic fuel cell (OMFC) that efficiently converts alcohols into carboxylic acids. This method may provide a way for the synthesis of fine chemicals from renewable resources under waste-free conditions.

Optical Switches

F. Bonardi, G. London,
N. Nouwen, B. L. Feringa,
A. J. M. Driessen* __________ 7234 – 7238

Light-Induced Control of Protein Translocation by the SecYEG Complex

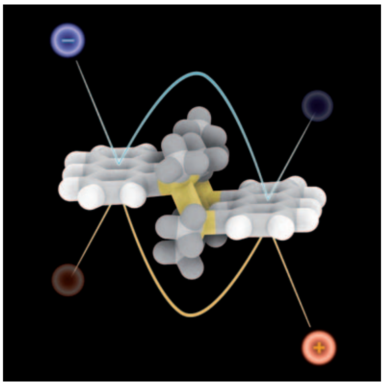


Please close the pore! An organochemical photoswitch was introduced into two transmembrane segments that comprise the lateral gate of the bacterial-membrane-embedded protein-conducting pore. Reversible switching of the azobenzene between the *trans* and *cis* configurations by irradiation with visible and UV light enforced the opening and closure of the protein-conducting pore (see scheme).

Organic Materials

W. Nakanishi, S. Hitosugi, A. Piskareva, Y. Shimada, H. Taka, H. Kita, H. Isobe* ———— **7239 – 7242**

Disilanyl Double-Pillared Bisanthracene: A Bipolar Carrier Transport Material for Organic Light-Emitting Diode Devices

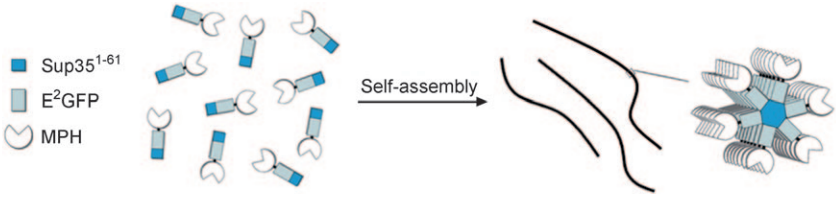


A step for “two-in-one”! A steplike molecule (see picture) was synthesized as a carrier transport material for layered OLED devices. This double-pillared molecule combines the π system of aromatic hydrocarbons with the σ system of silicon in a single structure and transports both holes and electrons in a device.

Biosensors

Y. Leng, H. P. Wei, Z. P. Zhang, Y. F. Zhou, J. Y. Deng, Z. Q. Cui, D. Men, X. Y. You, Z. N. Yu, M. Luo, X. E. Zhang* ———— **7243 – 7246**

Integration of a Fluorescent Molecular Biosensor into Self-Assembled Protein Nanowires: A Large Sensitivity Enhancement

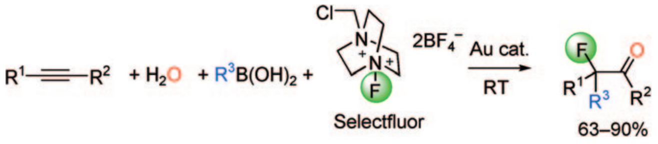


Wire to wire: The hybrid Sup35$^{1-61}$-E^{2}GFP-MPH, which consists of the pH-sensitive green fluorescent protein E^{2}GFP, the enzyme methyl parathion hydrolase (MPH), and the yeast prion protein Sup35$^{1-61}$ was obtained by gene fusion. A self-assembled nanowire was formed through aggregation of the Sup35$^{1-61}$ subunit (see picture). The wire acts as a biosensor that can detect methyl parathion with a sensitivity 10000 times greater than free E^{2}GFP-MPH.

Oxidative Gold Catalysis

W. Wang, J. Jasinski, G. B. Hammond,* B. Xu* ———— **7247 – 7252**

Fluorine-Enabled Cationic Gold Catalysis: Functionalized Hydration of Alkynes

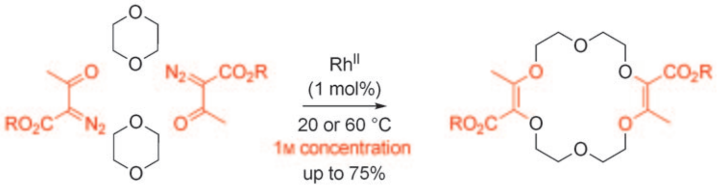


Fluorine makes it possible: A cationic fluorine–gold species generated by fluorination of a low-valence gold complex mediates the “functionalized hydration” of alkynes. A triple bond is used to install a carbonyl group and two new bonds on the α-carbon atom, all occurring in one pot, under mild conditions and in very good yields (see scheme).

Synthetic Methodology

W. Zeghida, C. Besnard, J. Lacour* ———— **7253 – 7256**

Rhodium(II)-Catalyzed One-Pot Four-Component Synthesis of Functionalized Polyether Macrocycles at High Concentration



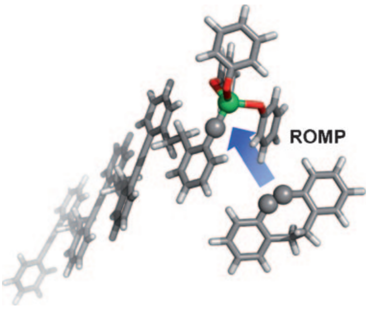
Against conventional wisdom, the rhodium(II)-catalyzed nontemplated macrocyclization of four separate components in one reaction vessel became more efficient as the concentration was increased. Thus, α-diazo-β-ketoesters underwent condensation with 1,4-dioxane, tetrahydrofuran, or tetrahydropyran as the solvent to yield 16- to 18-membered polyether macrocycles in up to 75 % yield (see scheme; R = Me, Et, PhCH$_2$CH$_2$, allyl, PhCH=CH$_2$).

Living Polymerization

F. R. Fischer,* C. Nuckolls* **7257 – 7260**

Design of Living Ring-Opening Alkyne Metathesis

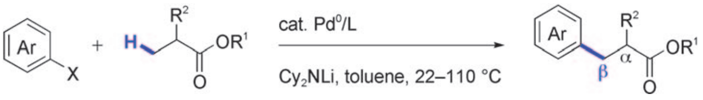
It's alive: A ring-strained alkyne based on dibenzo[*a*,*e*][8]annulene undergoes ring-opening metathesis polymerization (ROMP) to give a high-molecular-weight poly(*ortho*-phenylene) featuring alternating ethyl and ethynyl linkers along the polymer backbone. The molybdenum-alkylidyne-based catalyst system discriminates between strained and unstrained alkynes to yield a living polymer with an unparalleled low polydispersity.



C–H Functionalization

A. Renaudat, L. Jean-Gérard, R. Jazzar, C. E. Kefalidis, E. Clot,* O. Baudoin* **7261 – 7265**

Palladium-Catalyzed β Arylation of Carboxylic Esters



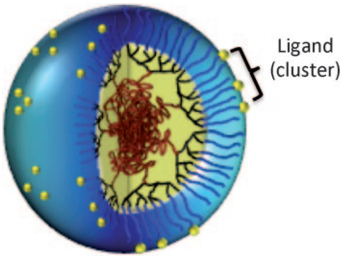
Alter ego: In the presence of an appropriate palladium(0) catalyst, carboxylic esters underwent β arylation instead of the more common α-arylation reaction with aryl halides containing an *ortho* electronegative substituent (see scheme; Cy = cyclohexyl). An asymmetric version of the reaction gave the product with an enantiomeric ratio of up to 77:23.

Nanoparticle Targeting

Z. Poon, S. Chen, A. C. Engler, H. Lee, E. Atas, G. von Maltzahn, S. N. Bhatia, P. T. Hammond* **7266 – 7270**

Ligand-Clustered "Patchy" Nanoparticles for Modulated Cellular Uptake and In Vivo Tumor Targeting

A matter of presentation: The manner in which polyvalent ligands are presented to a cell—homogeneously or in spatially defined groupings on a nanoparticle surface—may play an important role in cellular uptake. This aspect is investigated for the first time using a linear dendritic polymer construct to pattern the surfaces of nanoparticles with variable-sized ligand clusters in different spatial arrangements.

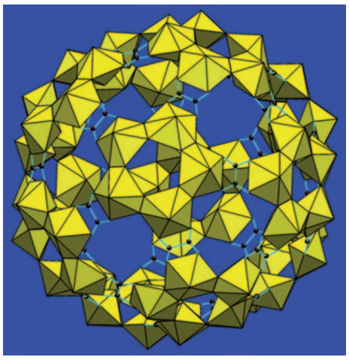


Polyoxometalates

J. Ling, C. M. Wallace, J. E. S. Szymanowski, P. C. Burns* **7271 – 7273**

Hybrid Uranium–Oxalate Fullerene Topology Cage Clusters

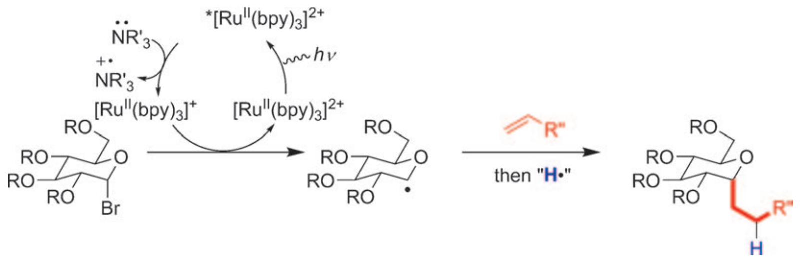
Fullerene's topology: Inorganic–organic hybrid cage clusters containing 36 and 60 uranyl peroxide polyhedra and 6 or 30 oxalate groups (see representation of a $\{U_{60}\}$ cluster) self-assemble in aqueous solution under ambient conditions. These clusters, which are derivatives of fullerene topologies, were crystallized for structure analysis, and are readily dissolved intact in water.



C-Glycosides

R. S. Andrews, J. J. Becker,
M. R. Gagné* ———— **7274 – 7276**

Intermolecular Addition of Glycosyl Halides to Alkenes Mediated by Visible Light

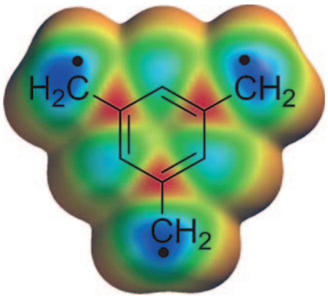


Catching photons: Visible light, an amine reductant, and a $[Ru(bpy)_3]^{2+}$ photocatalyst can be used to mediate the addition of glycosyl halides into alkenes to synthesize important C-glycosides (see scheme). This method shows the growing potential of photocatalysis to effectively drive useful and difficult chemical transformations.

Radicals

P. Neuhaus, W. Sander* —— **7277 – 7280**

Isolation and Characterization of the Triradical 1,3,5-Trimethylenebenzene

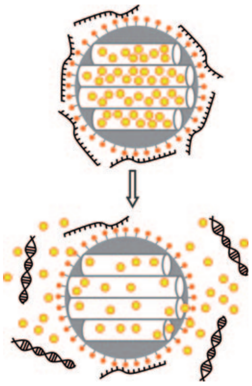


The highly symmetrical quartet triradical trimethylenebenzene has been isolated for the first time (see structure). Despite its open-shell character, it was photochemically stable and this makes it a promising building block for magnetic materials.

Functional Nanoparticles

E. Climent, R. Martínez-Máñez,*
F. Sancenón, M. D. Marcos, J. Soto,
A. Maquieira, P. Amorós —— **7281 – 7283**

Controlled Delivery Using Oligonucleotide-Capped Mesoporous Silica Nanoparticles

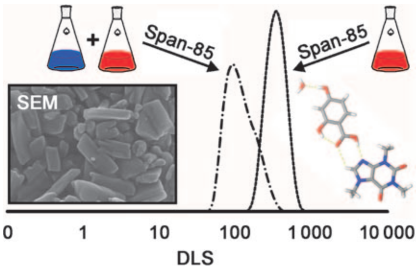


Caps off! A single-stranded oligonucleotide capped the pores on the surface of a silica mesoporous support, which contained an entrapped guest. In the presence of a complementary strand, the "molecular lock" on the delivery vehicle was opened and the entrapped guests were selectively released.

Nanostructures

J. R. G. Sander, D.-K. Bučar,
R. F. Henry, G. G. Z. Zhang,*
L. R. MacGillivray* ———— **7284 – 7288**

Pharmaceutical Nano-Cocrystals: Sonochemical Synthesis by Solvent Selection and Use of a Surfactant



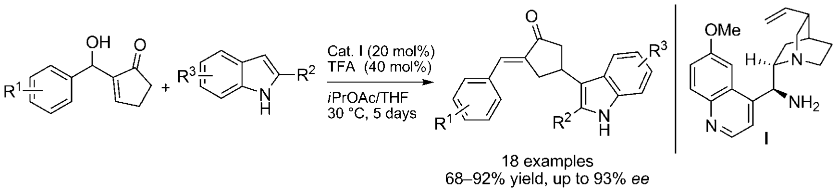
Nanopharmaceutics: Sonochemistry and the use of a surfactant (Span-85) was introduced to generate pharmaceutical cocrystals of nanometer-scale dimensions. This method overcomes the inherent solubility difference between the pharmaceutical agent (caffeine in this case) and the cocrystal former (2,4-dihydroxybenzoic acid; see picture).

Contents

Homogeneous Catalysis

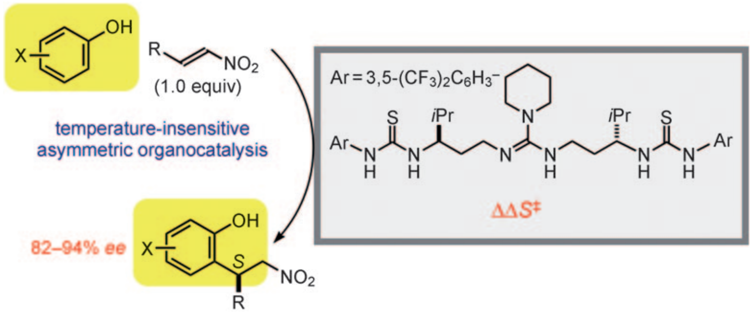
Working together: The title reaction proceeds in the presence of a thiolate-bridged diruthenium complex (**2**) and a secondary amine (**1**) to give the corresponding propargylic alkylated products in excellent yields as a mixture of two diastereoisomers, each with high enantioselectivity. The two catalysts activate propargylic alcohols and aldehydes, respectively, and cooperatively promote the enantioselective reaction.

Synthetic Methods



The unexpected becomes possible: The first enantioselective, direct nucleophilic substitution of Morita–Baylis–Hillman alcohols has been developed through the use of iminium catalysis. Unexpected δ-substituted products were obtained with exclusive regioselectivity and high enantioselectivity for the reaction of cyclopent-2-enone-derived alcohols with indoles catalyzed by **1**.

Synthetic Methods

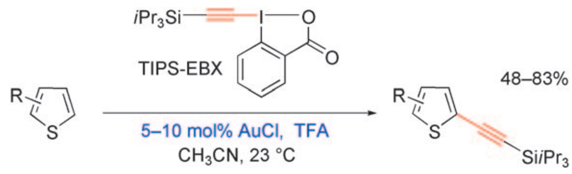


Soft and weak cooperation: Conformationally flexible organic compounds were found to promote the title transformation. These “soft” organocatalysts, which are able to control processes through the differential activation entropies $(\Delta\Delta S^{\ddagger}_{S-R})$ of the reactive intermediates, lead to high stereoselectivities without the requirement of fine-tuning the reaction temperatures (see scheme).

Cooperative Catalysis

J. P. Brand, J. Waser* ______ **7304 – 7307**

Direct Alkynylation of Thiophenes: Cooperative Activation of TIPS–EBX with Gold and Brønsted Acids

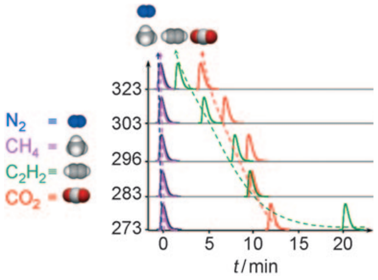


United we stand! Cooperative activation of the hypervalent-iodine reagent TIPS-EBX with a gold catalyst and a Brønsted acid allowed the first direct ethynylation of thiophenes at room temperature (see scheme; TFA = trifluoroacetic acid). The obtained ethynylthiophenes are important building blocks for organic dyes and electronic materials.

Metal–Organic Frameworks

E. Quartapelle Procopio, F. Linares, C. Montoro, V. Colombo, A. Maspero, E. Barea, J. A. R. Navarro* __ **7308 – 7311**

Cation-Exchange Porosity Tuning in Anionic Metal–Organic Frameworks for the Selective Separation of Gases and Vapors and for Catalysis

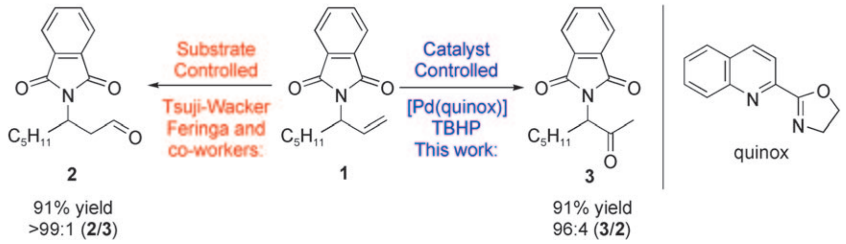


Temperature matters! The separation efficiency of complex mixtures of gases (acetylene, carbon dioxide, methane, nitrogen) and vapors (benzene, cyclohexane) by adsorption on A[Cu$_3$(μ_3-OH)(μ_3-4-carboxypyrazolato)$_3$] (A@**1**) metal–organic frameworks depends on temperature and the extraframework cation A (see picture). NH$_4$@**1** also behaves as an oxidation catalyst.

Synthetic Methods

B. W. Michel, J. R. McCombs, A. Winkler, M. S. Sigman* ______ **7312 – 7315**

Catalyst-Controlled Wacker-Type Oxidation of Protected Allylic Amines



On the contrary: Utilizing the [Pd(quinox)]–TBHP catalyst system, protected allylic amines were oxidized with high selectivity for the methyl ketone product. This is contrary to the results obtained by the substrate-controlled Tsuji–Wacker oxidation, which highlights the catalyst-controlled system presented here (see scheme). A variety of N-protecting groups undergo selective oxidation with high ketone selectivity. TBHP = *tert*-butylhydroperoxide.

C–H Activation

X.-F. Wu, P. Anbarasan, H. Neumann, M. Beller* ______ **7316 – 7319**

Palladium-Catalyzed Carbonylative C–H Activation of Heteroarenes

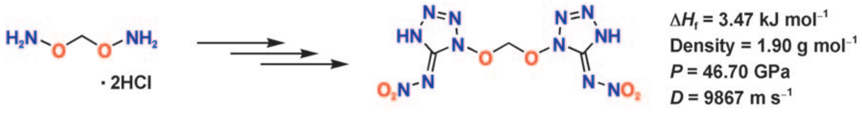
Not only carbonylation: The first carbonylative cross-coupling reactions towards ketones using C–H activation have been developed. Various heteroarenes, such as oxazoles, thiazoles, and imidazoles were used as coupling partners in this methodology. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, dppp = 1,3-bisdiphenylphosphinopropane, DMF = *N*,*N*-dimethylformamide.

Contents

Energetic Materials

Y.-H. Joo, J. M. Shreeve* ____ 7320 – 7323

High-Density Energetic Mono- or Bis(Oxy)-5-Nitroiminotetrazoles

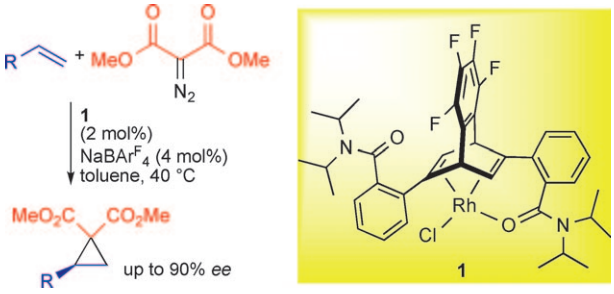


Making an impact: Oxy-5-aminotetrazoles, which were obtained from the reaction of cyanogen azide and alkyl oxyamine in 100% nitric acid (see scheme), give a series of highly energetic oxy-5-nitroiminotetrazolates in good yield. These compounds exhibit good physical and detonation properties, such as moderate thermal stabilities, high densities, high endothermy, good detonation pressures *P*, and good detonation velocities *D*.

Cyclopropanation

T. Nishimura,* Y. Maeda,
T. Hayashi* ____ 7324 – 7327

Asymmetric Cyclopropanation of Alkenes with Dimethyl Diazomalonate Catalyzed by Chiral Diene–Rhodium Complexes

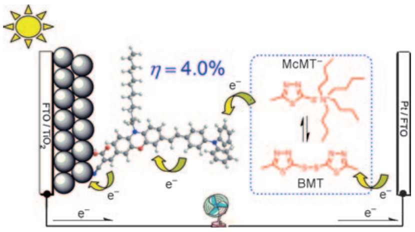


Chiral tridentate ligand: A chiral diene–rhodium complex (**1**; see scheme) was found to catalyze the intermolecular asymmetric cyclopropanation of alkenes with dimethyl diazomalonate to give 1,1-cyclopropane diesters in good yields and with high enantioselectivity.

Organic Electrolytes

H. Tian, X. Jiang, Z. Yu, L. Kloo,
A. Hagfeldt, L. Sun* ____ 7328 – 7331

Efficient Organic-Dye-Sensitized Solar Cells Based on an Iodine-Free Electrolyte

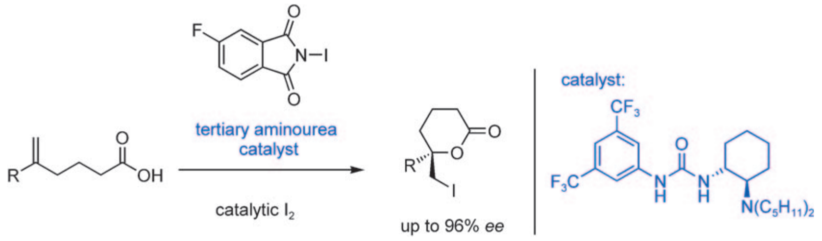


Deiodized salt: An organic redox couple (McMT⁻/BMT) was adopted for application in dye-sensitized solar cells. Based on a low-cost organic dye, TH305, an efficiency of 4.0% was achieved under simulated sunlight (100 mW cm⁻²). Photoelectrochemical measurements provided insights into the difference between the organic redox couple and traditional iodine-based electrolytes.

Asymmetric Catalysis

G. E. Veitch,
E. N. Jacobsen* ____ 7332 – 7335

Tertiary Aminourea-Catalyzed Enantioselective Iodolactonization

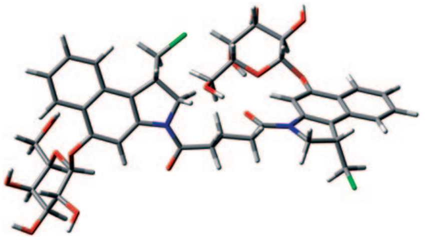


Binding the anion: A highly enantioselective iodolactonization of 5-hexenoic acids has been achieved using a tertiary aminourea-catalyst (see scheme). The use of catalytic iodine in this process is critical to enhancing both the reactivity and enantioselectivity of the stoichiometric I⁺ source. The mechanism is proposed to involve binding of an iodonium imidate intermediate by the H-bond donor catalyst.

Prodrugs

L. F. Tietze,* J. M. von Hof, M. Müller,
B. Krewer, I. Schuberth ____ **7336 – 7339**

Glycosidic Prodrugs of Highly Potent Bifunctional Duocarmycin Derivatives for Selective Treatment of Cancer

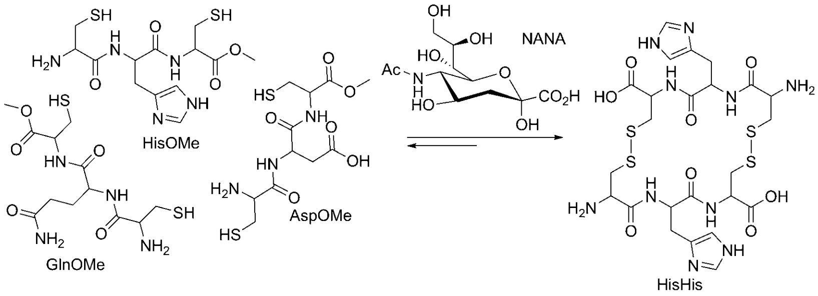


Cytotoxicities almost a million times lower than the prevailing active compounds, which can have IC_{50} values of about 100 fM, are displayed by new glycosidic prodrugs for selective tumor therapy (see example; gray C, white H, green Cl, blue N, red O). The cytotoxicity of these new active compounds is presumably not attributable to DNA intra- or DNA interstrand cross-linking, but might be based on an as yet unknown mechanism.

Molecular Recognition

M. Rauschenberg, S. Bomke, U. Karst,
B. J. Ravoo* ____ **7340 – 7345**

Dynamic Peptides as Biomimetic Carbohydrate Receptors

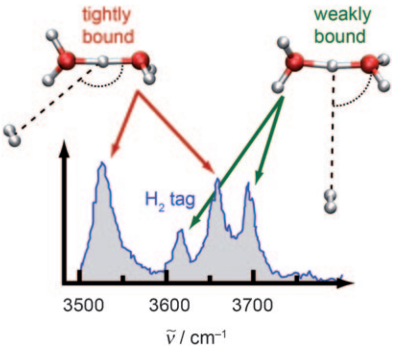


Finding the needle in the haystack: A dynamic combinatorial library (DCL) of peptides was created using the disulfide-exchange reaction of cysteines. Three cyclic peptides were found to be selective receptors for carbohydrates in water. One of these, HisHis, formed preferentially in a DCL in the presence of the neurotransmitter NANA.

Cation Solvation

M. Baer, D. Marx,
G. Mathias* ____ **7346 – 7349**

Theoretical Messenger Spectroscopy of Microsolvated Hydronium and Zundel Cations



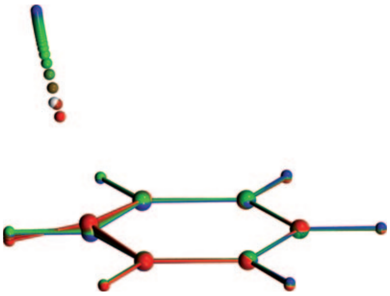
Water clusters revisited: The vibrational predissociation spectra of microsolvated Zundel cations has been an experimental and theoretical puzzle for more than two decades. Now it can be shown that the influence of tagging with H_2 can be understood in terms of a superposition of tightly bound and weakly bound adduct species, which offers a concise interpretation of the experimental action spectra.

Tunneling

T. P. M. Goumans,*
J. Kästner 7350–7352

Hydrogen-Atom Tunneling Could Contribute to H_2 Formation in Space

Cosmic cat.: Tunneling effects in the reaction between hydrogen atoms and benzene have been studied with a new direct dynamics implementation of harmonic quantum transition-state theory. In certain regions of interstellar space, tunneling could facilitate H chemisorption on polycyclic aromatic hydrocarbons, thereby catalyzing HD and H_2 formation.



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

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Service

Corrigendum

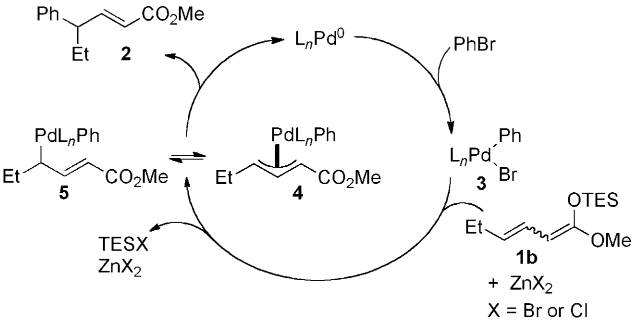
Palladium-Catalyzed γ-Arylation of α,β-Unsaturated Esters from Silyl Ketene Acetals

D. S. Huang, J. F. Hartwig* **5757–5761**

Angew. Chem. Int. Ed. **2010**, *49*

DOI 10.1002/anie.201002328

In Scheme 1 of this Communication (DOI: 10.1002/anie.201002328), one reagent was mistakenly omitted. The correct scheme is provided below.



Scheme 1. Potential mechanism for the coupling of **1b** with PhBr. TES = triethylsilyl.