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:

*X. Xu, M. Su Han, C. A. Mirkin**
A Gold Nanoparticle-Based, Real-Time Colorimetric Screening Method for Endonuclease Activity and Inhibition

*De Gao, H. Xu, M. A. Philbert, R. Kopelman**
Ultrafine Hydrogel Nanoparticles: Synthetic Approach and Therapeutic Application in Living Cells

*P. Agarwal, N. A. Piro, K. Meyer, P. Müller, C. C. Cummins**
An Isolable and Monomeric Phosphorus Radical That Is Resonance-Stabilized by the Vanadium(IV/V) Redox Couple

*C. Chatterjee, R. K. McGinty, Jean-P. Pellois, T. W. Muir**
Auxiliary-Mediated Site-Specific Peptide Ubiquitylation

G. A. Pierce, S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, N. D. Coombs, D. J. Willock*
Cationic Terminal Aminoborylene Complexes: Controlled Stepwise Insertion into M–B and B–N Double Bonds

*K. Ono, M. Yoshizawa, T. Kato, K. Watanabe, M. Fujita**
Porphine Dimeric Assemblies in Organic-Pillared Coordination Cages

News

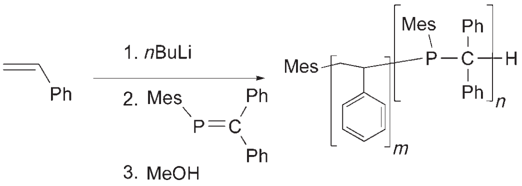
Books

Highlights

Inorganic Block Copolymers

I. Manners* ______ **1565–1568**

Block Copolymers with Functional Inorganic Blocks: Living Addition Polymerization of Inorganic Monomers



Doesn't have to be strictly organic to live: Living polymerizations of inorganic monomers provide a route to block copolymers that self-assemble in thin films or selective solvents to form functional nanodomains containing inorganic elements. An exciting addition to this field involves the recently reported living anionic addition polymerization of phosphaalkenes (see scheme; Mes = 2,4,6-$Me_3C_6H_2$).

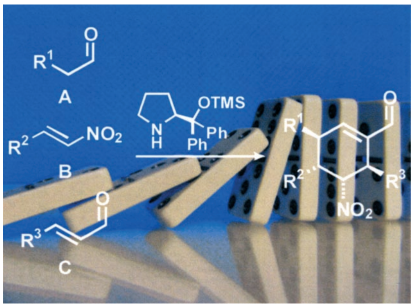
Minireviews

Domino Reactions

D. Enders,* C. Grondal, M. R. M. Hüttl ______ **1570–1581**

Asymmetric Organocatalytic Domino Reactions

Domino rally: Organocatalytic domino reactions are characterized by the efficient and stereoselective construction of complex molecules from simple precursors in a single process (see scheme; TMS = trimethylsilyl). This strategy circumvents the common drawbacks of classical synthesis, such as costly protecting-group strategies and lengthy purification procedures after each synthetic step.



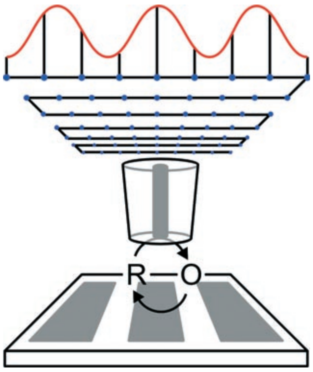
Contents

Reviews

Analytical Methods

G. Wittstock,* M. Burchardt, S. E. Pust,
Y. Shen, C. Zhao ______ **1584 – 1617**

Scanning Electrochemical Microscopy for Direct Imaging of Reaction Rates



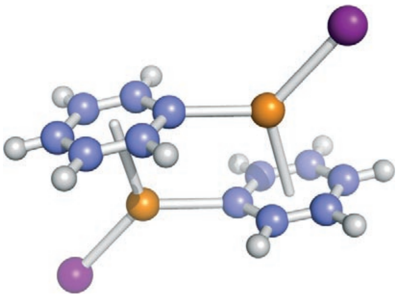
Scanning the horizon: Scanning electrochemical microscopy has become an indispensible tool for the investigation of localized processes at interfaces. The basics of this method will be detailed along with applications and perspectives in the areas of corrosion, surface technology, membrane processes, (bio)catalysis, as well as in biological and biochemical assays.

Communications

Organocalcium Compounds

R. Fischer, M. Gärtner, H. Görls,
L. Yu, M. Reiher,*
M. Westerhausen* ______ **1618 – 1623**

THF Solvates of Extremely Soluble Bis(2,4,6-trimethylphenyl)calcium and Tris(2,6-dimethoxyphenyl)dicalcium Iodide

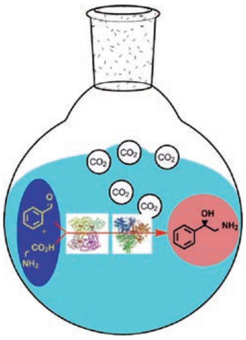


United for better solubility: A diaryl calcium compound could be isolated for the first time by fractionated crystallization of mesitylcalcium iodide. The aryl calcium iodide and diaryl calcium compounds show an extremely high solubility in THF even at -90 °C. Quantum chemical calculations point to dimerization or tetramerization through a novel η^6 coordination as a possible explanation (see picture; C mauve, H white, Ca orange, I purple).

Biocatalysis

J. Steinreiber, M. Schürmann, M. Wolberg,
F. van Assema, C. Reisinger, K. Fesko,
D. Mink, H. Griengl* ______ **1624 – 1626**

Overcoming Thermodynamic and Kinetic Limitations of Aldolase-Catalyzed Reactions by Applying Multienzymatic Dynamic Kinetic Asymmetric Transformations



Dynamic and successful: The asymmetric synthesis of 2-amino-1-phenylethanol was achieved by aminomethylation of benzaldehyde in the presence of the two enzymes L-threonine aldolase and L-tyrosine decarboxylase in a novel one-pot, two-enzyme process (see scheme). A modified method with three enzymes led to the enantioenriched amino alcohol in very high yield.

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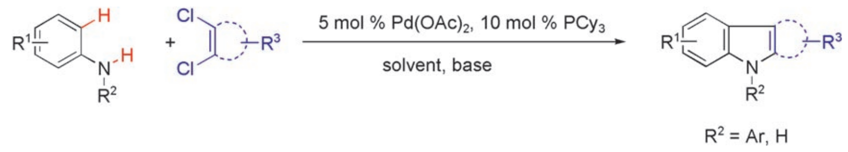
Domino Reactions

L. Ackermann,*
A. Althammer ——— **1627 – 1629**

Domino N–H/C–H Bond Activation: Palladium-Catalyzed Synthesis of Annulated Heterocycles Using Dichloro(hetero)arenes

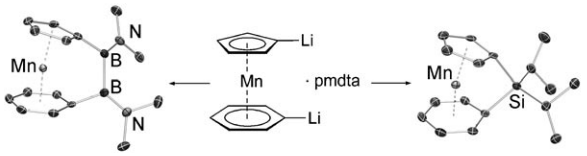


One after the other: A novel palladium-catalyzed domino reaction consisting of an amination and a direct C–H bond arylation allows for a general synthesis of annulated heterocycles starting from readily available 1,2-dichloroarenes and primary as well as secondary anilines (see scheme; Cy = cyclohexyl). This is highlighted by an efficient synthesis of the natural product murrayafoline A.

Ansa Complexes

H. Braunschweig,* T. Kupfer,
K. Radacki ——— **1630 – 1633**

Selective Dimetalation of $[Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$: Crystal Structure and Conversion to Strained [*n*]Metalloarenophanes

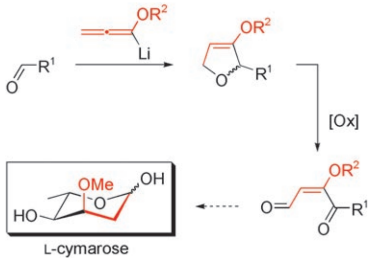


The heteroleptic sandwich complex $[Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ was selectively dilithiated with BuLi/pmdta to afford the highly reactive derivative $[Mn(\eta^5\text{-}C_5H_4Li)(\eta^6\text{-}C_6H_5Li)]\cdot$pmdta, which was structurally characterized by X-ray diffraction (pmdta = pentamethyldiethylenetriamine). Reactions with element dihalides yielded the corresponding [2]borametalloarenophane and [1]silametalloarenophane in good yields (see scheme).

Carbohydrates

M. Brasholz, H.-U. Reissig* **1634 – 1637**

Oxidative Cleavage of 3-Alkoxy-2,5-dihydrofurans and its Application to the De Novo Synthesis of Rare Monosaccharides as Exemplified by L-Cymarose



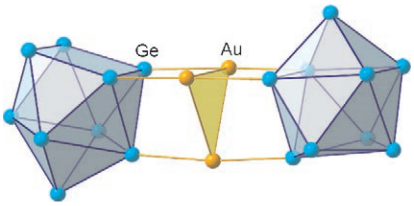
Donor-substituted α,β-unsaturated γ-keto aldehydes can be formed by the selective oxidative cleavage of 3-alkoxy-2,5-dihydrofurans. These 1,4-dicarbonyl compounds are highly suitable building blocks for the synthesis of rare sugars, for example, the dideoxypyranose L-cymarose (see scheme).

Cluster Compounds

A. Spiekermann, S. D. Hoffmann, F. Kraus,
T. F. Fässler* ——— **1638 – 1640**

$[Au_3Ge_{18}]^{5-}$—A Gold–Germanium Cluster with Remarkable Au–Au Interactions

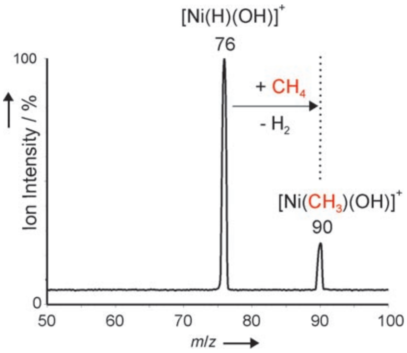
Gold linkers: The first soluble gold–germanium cluster was obtained from the reaction of $[Au(PPh_3)Cl]$ and K_4Ge_9. The formation of the gold complex $[Ge_9Au_3Ge_9]^{5-}$ (see picture) shows also an exciting result for gold chemistry: linearly coordinated gold atoms and the characteristics of aurophilic contacts between the metal atoms can be observed in the presence of polyanionic Zintl ions.



Cationic Gas-Phase Species

M. Schlangen, D. Schröder,* H. Schwarz* ______ 1641–1644

Pronounced Ligand Effects and the Role of Formal Oxidation States in the Nickel-Mediated Thermal Activation of Methane



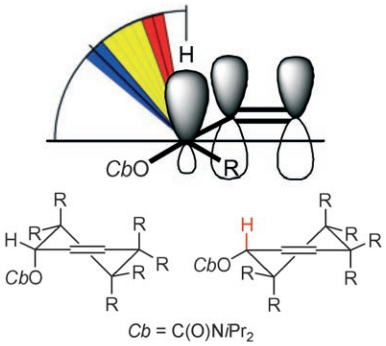
Related but different: The thermal activation of methane by cationic nickel complexes depends crucially on the nature of ligands and the formal oxidation state of the metal, as is illustrated by the isomeric water complexes: whereas $[Ni(H_2O)]^+$ is unreactive, the Ni^{III} isomer $[Ni(H)(OH)]^+$ activates the C–H bond in methane.

C–H Acidity

J. Becker, S. Grimme,* R. Fröhlich, D. Hoppe* ______ 1645–1649

Estimation of the Kinetic Acidity from Substrate Conformation—Stereochemical Course of the Deprotonation of Cyclohexenyl Carbamates

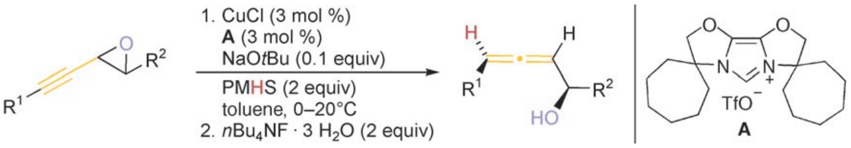
Get the bends: The kinetic C–H acidity of cyclohex-2-enyl carbamates is dependent on the torsion angle between the α C–H bond and the π system of the adjacent double bond. A deprotonation study and DFT calculations of the activation energies for lithiation show that the ease of deprotonation is predictable from a conformational analysis of the substrates. Furthermore, the stereochemical course of substitution reactions was determined.



Copper Hydride Catalysis

C. Deutsch, B. H. Lipshutz, N. Krause* ______ 1650–1653

Small but Effective: Copper Hydride Catalyzed Synthesis of α-Hydroxyallenes

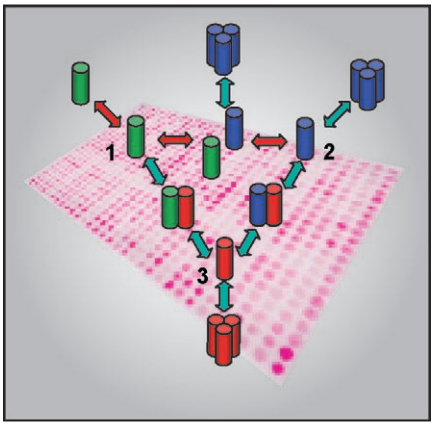


Mild and efficient: The copper hydride catalyzed diastereoselective S_N2' reduction of propargyl oxiranes provides α-hydroxyallenes bearing various functional groups (ethers, esters, alcohols; see scheme, PMHS = polymethylhydridosiloxane). The best results were obtained with a copper hydride catalyst and an N-heterocyclic carbene ligand. The resulting allenes are useful substrates, as they undergo, for example, regio- and chemoselective cycloisomerization to give 2,5-dihydrofurans.

Protein Structures

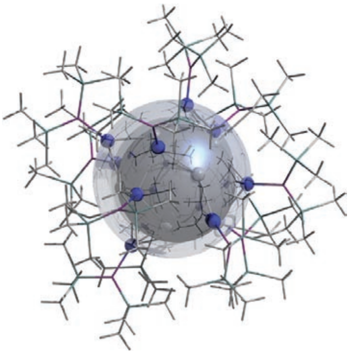
M. Portwich, S. Keller, H. M. Strauss, C. C. Mahrenholz, I. Kretzschmar, A. Kramer, R. Volkmer* ______ 1654–1657

A Network of Coiled-Coil Associations Derived from Synthetic GCN4 Leucine-Zipper Arrays



Two is better than one: Coiled-coil sequence motifs are versatile protein–protein interaction modules. Single and double substitutions of the GCN4 coiled coil (**1**, **2**, and **3**) showed that the core positions **a** and **d** in the third heptad act as a switch for the transition from the native homodimeric to homotrimeric structures. This creates a synthetic three-membered association network with monomeric, homotrimeric, and heterodimeric coiled-coil states.

Not a bird, not a plane, perhaps a superatom: The term “superatom” has been used for “naked” metal atom clusters with a certain electronic structure. On the basis of structural data the question of whether this classification—the Jellium model—is a suitable description of a metalloid cluster with the same number of valence electrons is addressed. The picture shows the superatomic core of naked and ligand-bearing Ga atoms in the title cluster.



Cluster Compounds

J. Hartig, A. Stößer, P. Hauser, H. Schnöckel* ———— 1658 – 1662

A Metalloid $[Ga_{23}\{N(SiMe_3)_2\}_{11}]$ Cluster: The Jellium Model Put to Test

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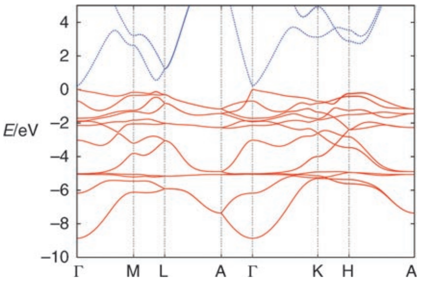


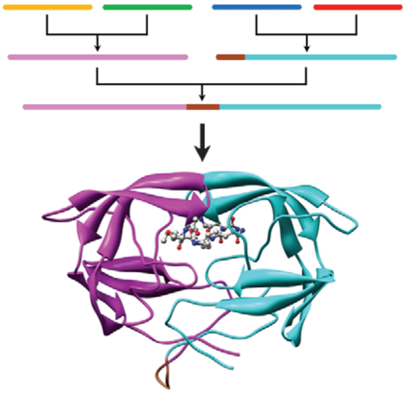
Super heavy: According to relativistic Dirac–Kohn–Sham calculations, eka-mercury (element 112) is a semiconductor in the solid state (see band structure; red: filled bands, blue: empty bands). In the absence of relativistic effects, condensed eka-mercury would be a hexagonal close-packed metal similar to zinc and cadmium.

Element 112

N. Gaston, I. Opahle, H. W. Gäggeler, P. Schwerdtfeger* ———— 1663 – 1666

Is Eka-Mercury (Element 112) a Group 12 Metal?

Synthesizing enzymes: The great potential of recently developed methods for the fully convergent chemical synthesis of proteins has been demonstrated by the synthesis of the 203 amino acid “covalent dimer” HIV-1 protease (see picture). The 21 870 Da protein synthesized has full enzymatic activity and the correct three-dimensional structure, as demonstrated by high-resolution X-ray crystallographic analysis.



Enzyme Total Synthesis

V. Yu. Torbeev, S. B. H. Kent* ———— 1667 – 1670

Convergent Chemical Synthesis and Crystal Structure of a 203 Amino Acid “Covalent Dimer” HIV-1 Protease Enzyme Molecule

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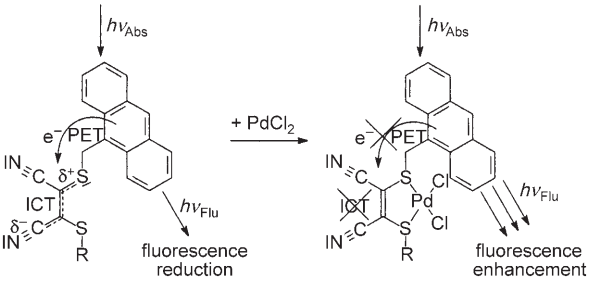


When push comes to shove: The oxidative photoinduced electron transfer (PET) in anthrylmethylthiomaleonitrile derivatives is regulated by the intramolecular charge transfer (ICT) of the “push–pull” dithiomaleonitrile receptor. Selective complexation with palladium chloride switches off the ICT, stops the PET, and results in fluorescence enhancement (see picture).

Molecular Sensors

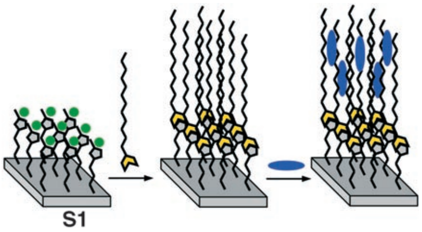
T. Schwarze, H. Müller, C. Dosche, T. Klamroth, W. Mickler, A. Kelling, H.-G. Löhmannsröben, P. Saalfrank, H.-J. Holdt* ———— 1671 – 1674

Luminescence Detection of Open-Shell Transition-Metal Ions by Photoinduced Electron Transfer Controlled by Internal Charge Transfer of a Receptor

Surfactant Detection

C. Coll, R. Martínez-Máñez,*
M. D. Marcos, F. Sancenón,*
J. Soto ———— **1675–1678**

A Simple Approach for the Selective and Sensitive Colorimetric Detection of Anionic Surfactants in Water



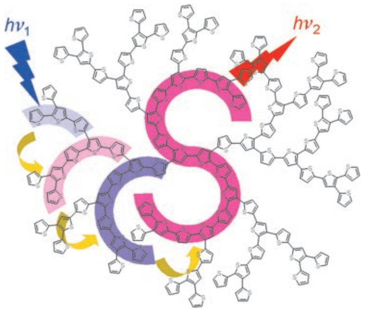
Good color sense: A sensing material (**S1**) containing imidazolium-anchored binding groups is used with a suitable dye (methylene blue) in a simple two-step protocol for the colorimetric detection of anionic surfactants in water (see picture). A detection limit of 1 ppm can be achieved, and the method is free from the use of hazardous solvents.

Conjugated Dendrimers

C.-Q. Ma, E. Mena-Osteritz,
T. Debaerdemaeker, M. M. Wienk,
R. A. J. Janssen, P. Bäuerle* **1679–1683**

Functionalized 3D Oligothiophene Dendrons and Dendrimers—Novel Macromolecules for Organic Electronics

Family tree: Novel functionalized dendritic oligothiophenes up to a fourth generation have been prepared. The highly soluble and structurally defined macromolecules show promising optoelectronic properties and performance in organic photovoltaic devices.

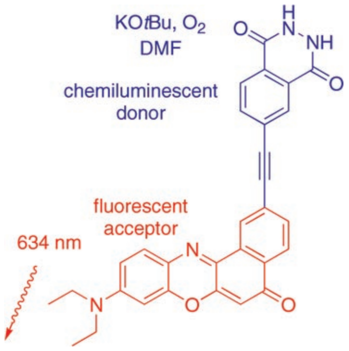


Chemiluminescence

J. Han, J. Jose, E. Mei,
K. Burgess* ———— **1684–1687**

Chemiluminescent Energy-Transfer Cassettes Based on Fluorescein and Nile Red

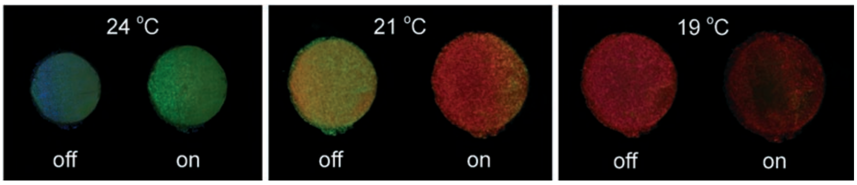
The long and the short of it: Luminol chemiluminesces with a beautiful blue color; however, to be useful for biotechnological applications, the emission must be shifted to much longer wavelengths. Energy-transfer cassettes like that shown in the picture provide one solution.



Polymer Gels

K. Matsubara, M. Watanabe,*
Y. Takeoka* ———— **1688–1692**

A Thermally Adjustable Multicolor Photochromic Hydrogel



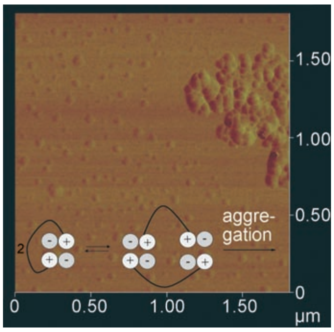
A rainbow of possibilities: A porous polymer gel undergoes light-triggered rapid two-state switching between two arbitrary structural colors at a controlled temperature (see picture; "on": upon UV irradiation, "off": in the dark). This switching is attributed to a change between two volume states. As the temperature also contributes to the degree of swelling of the gel, the color of the gel can be tuned thermally over a wide range of wavelengths.

Supramolecular Nanostructures

C. Schmuck,* T. Rehm, K. Klein, F. Gröhn ——— 1693 – 1697

Formation of Vesicular Structures through the Self-Assembly of a Flexible Bis-Zwitterion in Dimethyl Sulfoxide

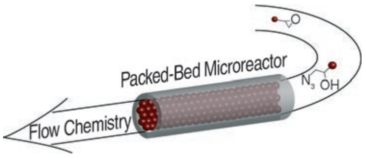
Small molecule, large structures: The connection of two zwitterionic binding motifs with a lipophilic alkyl linker results in an amphiphilic bis-zwitterion, which forms self-assembled vesicles even in polar solutions. The data suggest that two bis-zwitterions dimerize and then further aggregate to form vesicles, most likely driven by H-bonding and van der Waals interactions between the linkers.



Microreactors

A. R. Bogdan, B. P. Mason, K. T. Sylvester, D. T. McQuade* ——— 1698 – 1701

Improving Solid-Supported Catalyst Productivity by Using Simplified Packed-Bed Microreactors



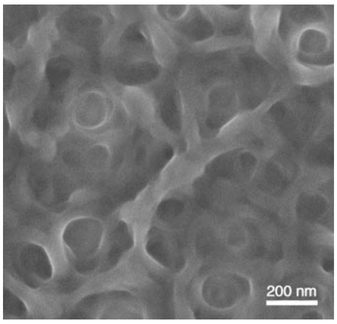
Going with the flow: Packed-bed microreactors are formed from polymeric tubing and a resin-supported catalyst. By using supported catalysts in flow systems, productivity and recycling are greatly improved. This approach can be used to couple multiple catalysts together for generating complex molecules in one flow-through process.

Macroporous Structures

Y. Ma, W.-F. Dong,* M. A. Hempenius, H. Möhwald, G. J. Vancso* ——— 1702 – 1705

Layer-by-Layer Constructed Macroporous Architectures

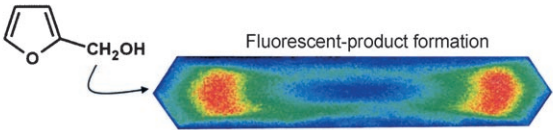
Bottoms up! Films were built up in a layer-by-layer fashion using high-molar-mass double-stranded DNA and cationic poly(ferrocenylsilane) polyelectrolytes. In this one-step "bottom-up" self-assembly approach, a unique macroporous architecture (see picture) featuring biocompatible and redox-active components was obtained.



Zeolites

M. B. J. Roeffaers, B. F. Sels, H. Uji-i, B. Blanpain, P. L'hoëst, P. A. Jacobs, F. C. De Schryver, J. Hofkens, D. E. De Vos* ——— 1706 – 1709

Space- and Time-Resolved Visualization of Acid Catalysis in ZSM-5 Crystals by Fluorescence Microscopy

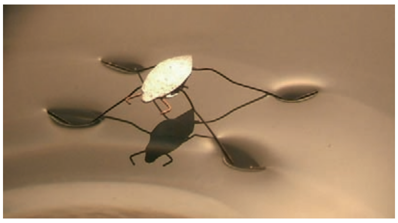


ZSM-5 at work: Acid-catalyzed condensation of furfuryl alcohol in the pores of zeolite ZSM-5 was followed under the fluorescence microscope. During the lifetime of a catalyst, from the reaction start to deactivation, the reactivity of the different crystal segments varies. The technique allows the heterogeneity of activity within individual crystals to be visualized (see picture).

Surface Chemistry

I. A. Larmour, S. E. J. Bell,*
G. C. Saunders ________ **1710–1712**

Remarkably Simple Fabrication of Superhydrophobic Surfaces Using Electroless Galvanic Deposition



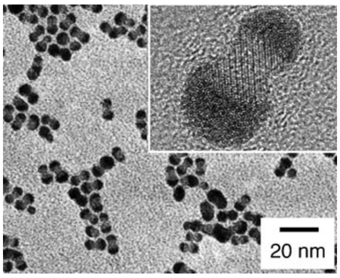
Superhydrophobic surfaces with contact angles between 173° and 180° can be produced simply by spontaneous deposition of a textured gold or silver coating layer, followed by a self-assembled monolayer of polyfluoroalkyl thiol. Objects of any size or shape may be coated. For example, the metal "pond skater" (photo) stands on superhydrophobic copper legs.

Nanostructures

T. Teranishi,* M. Saruyama, M. Nakaya,
M. Kanehara ________ **1713–1715**

Anisotropically Phase-Segregated Pd–Co–Pd Sulfide Nanoparticles Formed by Fusing Two Co–Pd Sulfide Nanoparticles

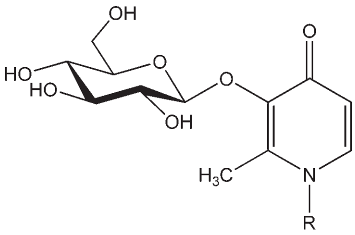
As nutty as a fruitcake! PdS_x seed-mediated growth has led to the formation of heterostructured Pd–Co–Pd sulfide peanut-shaped nanoparticles, which were generated by fusing two Co–Pd sulfide acorn-shaped nanoparticles with the Co_9S_8 phases aligned in the same crystallographic orientation (see TEM image).



Prodrugs

H. Schugar,* D. E. Green, M. L. Bowen,
L. E. Scott, T. Storr, K. Böhmerle,
F. Thomas, D. D. Allen, P. R. Lockman,
M. Merkel, K. H. Thompson,
C. Orvig* ________ **1716–1718**

Combating Alzheimer's Disease With Multifunctional Molecules Designed for Metal Passivation

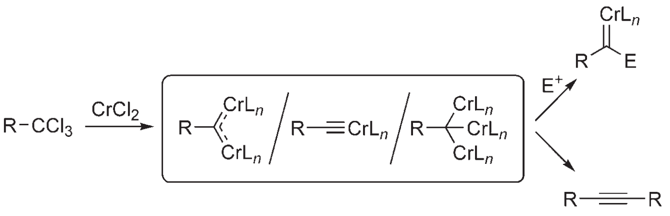


A trifunctional approach: 3-hydroxy-4-pyridinones that contain phenol groups for antioxidant functionality are further elaborated with pendant glucosyl moieties for improved blood–brain barrier targeting (see structure; R = phenyl, 4-hydroxyphenyl). Glycosidase removal of the carbohydrate substituents gives ligands that are ready to passivate excess metal ions, especially copper and zinc, in the brain. These molecules are potential prodrugs for treatment of neurodegenerative diseases, including Alzheimer's disease.

Synthesis Methods

R. Bejot, A. He, J. R. Falck,*
C. Mioskowski* ________ **1719–1722**

Chromium–Carbyne Complexes: Intermediates for Organic Synthesis

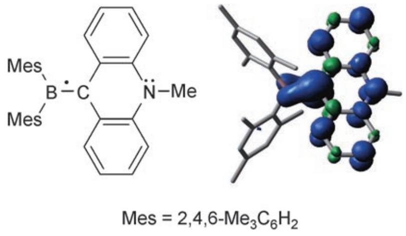


On the same route: Chromium-carbyne complexes are readily prepared by treatment of 1,1,1-trichloromethyl reagents with chromium(II) chloride. They serve as intermediates in the selective formation of a wide variety of products, such as alkynes, alkenes, β-hydroxy ketones, aldehydes, allylic alcohols, and allenes (see scheme, E = electrophile).

Carbon–Boron Radicals

C.-W. Chiu, F. P. Gabbaï* ____ 1723–1725

A 9-Borylated Acridinyl Radical

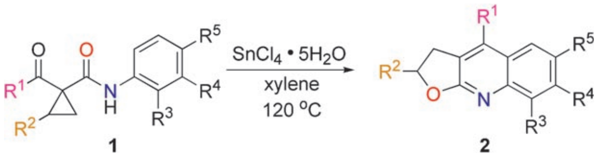


An odd molecule with an unpaired electron: Reduction of a cationic borane bearing an α-methylium center leads to the formation of a neutral radical, which has been studied by X-ray analysis and EPR spectroscopy. The computed spin density (see picture, right) of this radical shows substantial localization of the unpaired electron in a polarized B–C π-bonding orbital, a conclusion corroborated by an unusually short B–C bond.

Synthetic Methods

Z. Zhang, Q. Zhang,* S. Sun, T. Xiong,
Q. Liu* ____ 1726–1729

Domino Ring-Opening/Recyclization Reactions of Doubly Activated Cyclopropanes as a Strategy for the Synthesis of Furoquinoline Derivatives

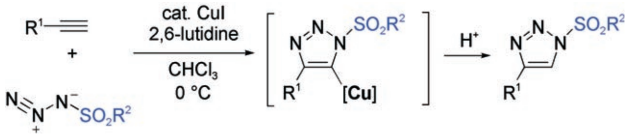


In one easy step, doubly activated cyclopropanes **1** can be transformed into furoquinoline derivatives **2** through a tandem ring-opening/recyclization reaction mediated by $SnCl_4 \cdot 5H_2O$. A variety of substrates **1** derived from cheap starting materials were converted into the corresponding furoquinolines in good to excellent yields with high chemo- and regioselectivity. R = H, Me, OMe, Cl, or aromatic group is naphthyl.

Synthetic Methods

E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae,
V. V. Fokin,* K. B. Sharpless,
S. Chang* ____ 1730–1733

Copper-Catalyzed Synthesis of *N*-Sulfonyl-1,2,3-triazoles: Controlling Selectivity

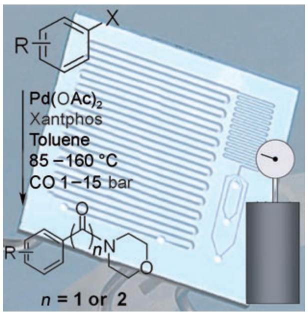


4-Substituted 1-(*N*-sulfonyl)-1,2,3-triazoles are selectively obtained by using the Cu-catalyzed azide–alkyne cycloaddition reaction with sulfonyl azides. Performing the reaction at 0 °C in chloroform in the presence of 2,6-lutidine and CuI as the catalyst effectively prevents the ketenimine pathway and provides convenient access to *N*-sulfonyltriazoles in good to excellent yields.

Microreactors

E. R. Murphy, J. R. Martinelli,
N. Zaborenko, S. L. Buchwald,*
K. F. Jensen* ____ 1734–1737

Accelerating Reactions with Microreactors at Elevated Temperatures and Pressures: Profiling Aminocarbonylation Reactions

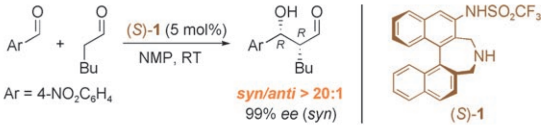


Squeeze play: Pressurized microreactor systems greatly expand the range of reaction conditions and accelerate gas–liquid mass transfer. Heck aminocarbonylation reactions (see scheme) exemplify the potential for the quick and safe scanning of reagents and reaction conditions. The yield of amide increases with an increase in temperature and the selectivity for α-ketoamide production (*n* = 2) increases at lower temperature and higher pressure.

Contents

Organocatalysis

T. Kano, Y. Yamaguchi, Y. Tanaka,
K. Maruoka* ———— **1738 – 1740**



syn-Selective and Enantioselective Direct Cross-Aldol Reactions between Aldehydes Catalyzed by an Axially Chiral Amino Sulfonamide

Complementary to proline: An axially chiral amino sulfonamide (*S*)-**1** was successfully applied as the catalyst to the direct cross-aldol reaction between two different aldehydes (see scheme; NMP = *N*-methylpyrrolidone). This catalyst has the advantage of giving mainly *syn* products, while proline shows the opposite *anti* selectivity.

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigendum

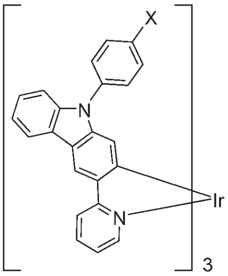
Multifunctional Iridium Complexes Based on Carbazole Modules as Highly Efficient Electrophosphors

W.-Y. Wong,* C.-L. Ho, Z.-Q. Gao, B.-X. Mi, C.-H. Chen, K.-W. Cheah, Z. Lin
———— **7800–7803**

Angew. Chem. Int. Ed. **2006**, *45*

DOI 10.1002/anie.200602906

Since publication of their Communication, it has been brought to the authors' attention that the chemical structures of **1** and **2** shown in Scheme 1 were incorrectly drawn. The authors apologize for the oversight. The correct structures are shown below.



fac-[Ir(X-Cz-py)$_3$]
X = H (**1**)
X = F (**2**)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