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:

*A. Asati, S. Santra, C. Kaittanis, S. Nath, J M. Perez**
Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles

L. Xu, C. E. Doubleday, K. N. Houk**
Dynamics of 1,3-Dipolar Cycloadditions of Diazonium Betaines with Acetylene and Ethylene: Bending Vibrations Facilitate Reaction

*P. Antoni, Y. Hed, A. Nordberg, D. Nyström, H. von Holst, A. Hult, M. Malkoch**
Bifunctional Dendrimers: From Robust Synthesis and Accelerated One-Pot Postfunctionalization Strategy to Potential Applications

*M. S. Nikolic, C. Olsson, A. Salcher, A. Kornowski, A. Rank, R. Schubert, A. Frömsdorf, H. Weller, S. Förster**
Micelle and Vesicle Formation of Amphiphilic Nanoparticles

*R. M. van der Veen, C. J. Milne, A. El Nahhas, F. A.Lima, V.-T. Pham, J. Best, J. A. Weinstein, C. N. Borca, R. Abela, C. Bressler, M. Chergui**
Structural Determination of a Photochemically Active Diplatinum Molecule by Time-Resolved EXAFS Spectroscopy

*G. Seidel, R. Mynott, A. Fürstner**
Elementary Steps of Gold Catalysis: NMR Spectroscopy Reveals the Highly Cationic Character of a Gold Carbenoid

*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

*G. E. Sigmon, D. K. Unruh, J. Ling, B. Weaver, M. Ward, L. Pressprich, A. Simonetti, P. C. Burns**
Symmetry Versus Minimal Pentagonal Adjacencies in Uranium-Based Polyoxometalate Fullerene Topologies

News


G. Férey


U. Bornscheuer


R. Zare

Inorganic Chemistry:
G. Férey ____ **1886**

Awarded Biocatalysis:
Prize to U. Bornscheuer ____ **1886**

Physical Chemistry:
R. Zare Honored ____ **1886**

Author Profile

"My biggest motivation is facing a new challenge. My favorite subject at school was geography…!"
These facts and more information about Christian Serre can be found on page 1887.

Christian Serre ____ **1887**

Books

Vanadium The Versatile Metal | Kenneth Kustin, João Costa Pessoa, Debbie C. Crans | *reviewed by R. K. O. Sigel* ____ **1888**

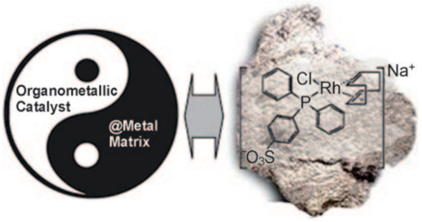
Contents

Highlights

Catalysis

A. Thomas,* M. Driess* ___ **1890 – 1892**

Bridging the Materials Gap in Catalysis: Entrapment of Molecular Catalysts in Functional Supports and Beyond

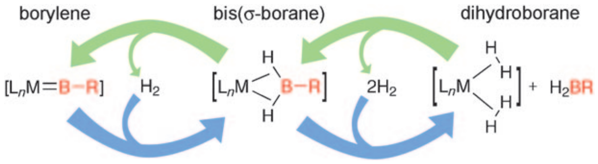


Rising sun of the materials world: Tremendous efforts are being made to combine the potential of molecular catalysts with that of functional supports. An approach towards unifying homogeneous and heterogeneous catalysis is the entrapment of organometallic catalysts in a metal matrix, which leads to well-defined composites that are suitable as heterogeneous catalysts for hydrogenation of styrene and diphenylacetylene.

Borylene Complexes

H. Braunschweig,*
R. D. Dewhurst ___ **1893 – 1895**

Reversible σ-Borane-to-Borylene Transformation: A Little Something For Everyone



A reaction with many facets: The facile dehydrogenative synthesis of a borylene complex (left in scheme) from a dihydroborane (right), proceeds reversibly at room-temperature. The implications of this reaction for the fields of inorganic, main-group, and hydrogen-storage chemistry are covered in this Highlight.

Hydroboration

S. P. Thomas,
V. K. Aggarwal* ___ **1896 – 1898**

Asymmetric Hydroboration of 1,1-Disubstituted Alkenes

A breakthrough in the asymmetric hydroboration of notoriously difficult 1,1-disubstituted alkenes using a new family of highly effective hydroboration reagents is described (see scheme). The intermediate boranes can be oxidized to alcohols or used in Suzuki–Miyaura cross-coupling reactions.

For the USA and Canada:
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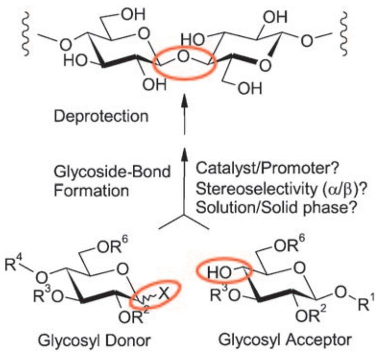
Reviews

Glycosidation

X. Zhu,* R. R. Schmidt* ____ **1900 – 1934**

New Principles for Glycoside-Bond Formation



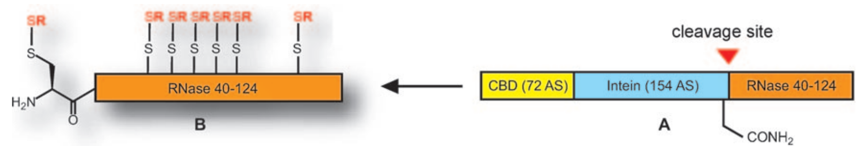
Meeting the demand for sugars: The importance of oligosaccharides and glycoconjugates in biological systems has stimulated a need to access significant amounts of these compounds. Much effort has been devoted to the stereoselective generation of the key glycosidic bond, both between carbohydrate residues (see scheme) and to the aglycone. Various methodologies are now available for the efficient synthesis of structurally defined complex oligosaccharides and glycoconjugates.

Communications

Glycosylation (1)

C. Piontek, P. Ring, O. Harjes, C. Heinlein, S. Mezzato, N. Lombana, C. Pöhner, M. Püttner, D. Varón Silva, A. Martin, F. X. Schmid, C. Unverzagt* **1936 – 1940**

Semisynthesis of a Homogeneous Glycoprotein Enzyme: Ribonuclease C: Part 1

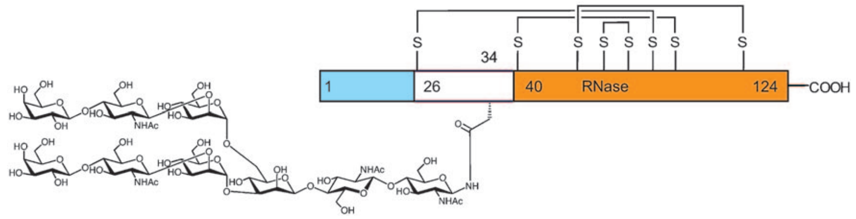


Seven in one blow: The efficient formation of mixed disulfides on the thiol-rich fusion protein **A** followed by subsequent intein cleavage gave the fragment **B** with all seven cysteines protected against oxidation. The native chemical ligation of **B** with synthetic glycopeptide thioesters provides glycoproteins.

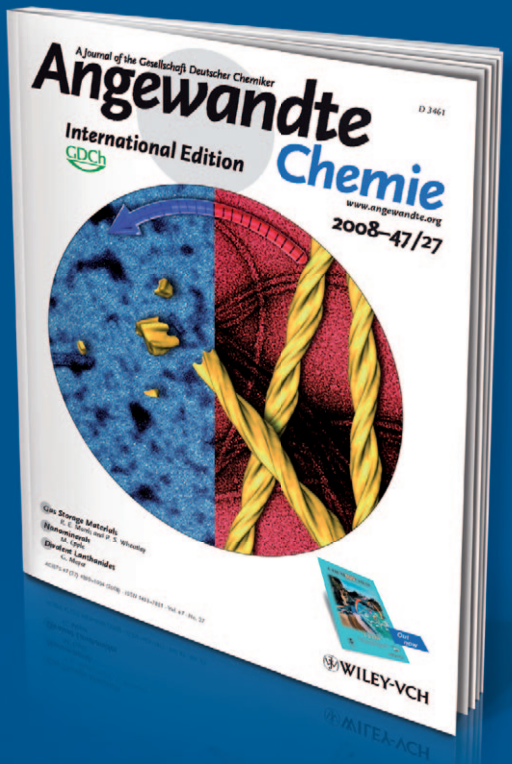
Glycosylation (2)

C. Piontek, D. Varón Silva, C. Heinlein, C. Pöhner, S. Mezzato, P. Ring, A. Martin, F. X. Schmid, C. Unverzagt* **1941 – 1945**

Semisynthesis of a Homogeneous Glycoprotein Enzyme: Ribonuclease C: Part 2



Active RNase glycoprotein from three pieces: The glycoprotein enzyme ribonuclease C, which contains a complex saccharide N-glycan, was synthesized by sequential native chemical ligation. An optimized ligation and isolation protocol allowed the efficient assembly and refolding of the 124 amino acid enzyme.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Chemie
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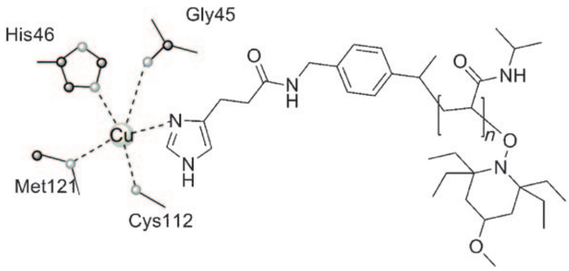
2008–47/27
D 3461
WILEY-VCH

Protein–Polymer Hybrids

N. Rosenberger, A. Studer,* N. Takatani,
H. Nakajima, Y. Watanabe* **1946–1949**

Azurin–Poly(*N*-isopropylacrylamide) Conjugates by Site-Directed Mutagenesis and their Thermosensitive Behavior in Electron-Transfer Processes

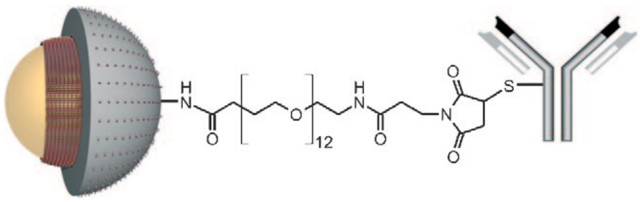


Searching for "intelligence": Azurin–PNIPAM conjugates were prepared by site-directed mutagenesis followed by protein reconstitution by using imidazole-conjugated poly(*N*-isopropylacrylamides). The polymer-bound imidazole acts as a ligand in the active site of the blue copper protein azurin. The bioconjugates showed thermosensitive behavior in electron-transfer processes with reduced cytochrome c.

Bioanalytical Methods

B. Küstner, M. Gellner, M. Schütz,
F. Schöppler, A. Marx, P. Ströbel, P. Adam,
C. Schmuck, S. Schlücker* **1950–1953**

SERS Labels for Red Laser Excitation: Silica-Encapsulated SAMs on Tunable Gold/Silver Nanoshells



In a glass house: Silica-encapsulated self-assembled monolayers (SAMs) on tunable gold/silver nanoshells were used as labels for surface-enhanced Raman scattering (SERS). This concept combines the spectroscopic advantages arising from maximum surface coverage and uniform molecular orientation of the Raman reporter molecules within the complete monolayer together with the high chemical and mechanical stability of the glass shell.

Charge-Transfer Complexes

G. Steinfeld, V. Lozan, H.-J. Krüger,
B. Kersting* **1954–1957**

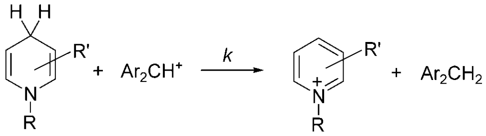
Trapping of a Thiolate→Dibromine Charge-Transfer Adduct by a Macrocyclic Dinickel Complex and Its Conversion into an Arenesulfenyl Bromide Derivative

Stuck on sulfur: The first transition-metal complexes with S–Br units are surprisingly stable. Solid **3** is stable for at least six months and under vacuum solid **2** does not lose Br_2. The formation of the first structurally characterized transition-metal arenesulfenyl bromide complex **3** occurs with a change of the spin ground state from $S=2$ to $S=0$.

Organocatalysis

D. Richter, H. Mayr* **1958–1961**

Hydride-Donor Abilities of 1,4-Dihydropyridines: A Comparison with π Nucleophiles and Borohydride Anions

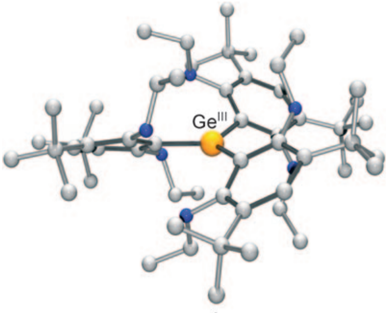


How are dihydropyridines like indoles? Both groups of compounds have similar nucleophilicity parameters *N* and are therefore suitable substrates for iminium-catalyzed reactions of α,β-unsaturated aldehydes. The *N* parameters of 1,4-dihydropyridines were derived from the rates of hydride transfer reactions to benzhydrylium ions (see scheme).

Stable Germanium Radicals

C. Drost,* J. Griebel, R. Kirmse,
P. Lönnecke, J. Reinhold ___ **1962 – 1965**

A Stable and Crystalline Triarylgermyl Radical: Structure and EPR Spectra



1

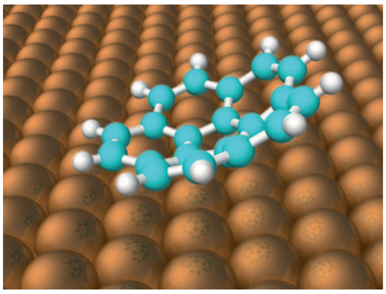
A radical thing: After being obtained unexpectedly in low yields, the synthesis of the first stable triarylgermyl radical $^{\bullet}Ge[3,5\text{-}tBu_2\text{-}2,6\text{-}(EtO)_2C_6H]_3$ (**1**; C gray, O blue) was considerably optimized, and the product was investigated by X-ray analysis and EPR spectroscopy. The results were compared with DFT-MO studies for the model compound $^{\bullet}Ge[2,6\text{-}(MeO)_2C_6H_3]$.

Polymorphism

L. Merz, M. Parschau, L. Zoppi,
K. K. Baldridge, J. S. Siegel
K.-H. Ernst* ___ **1966 – 1969**

Reversible Phase Transitions in a Buckybowl Monolayer

Like penguins on ice, buckybowl molecules move closer together when cooled on a copper surface (see model of a corannulene molecule adsorbed on Cu(111)). Upon heating, the molecules spread out into the original crystal phase again. The lower density at room temperature can be explained by the increase in entropy owing to the excitation of bowl vibrations at the surface.

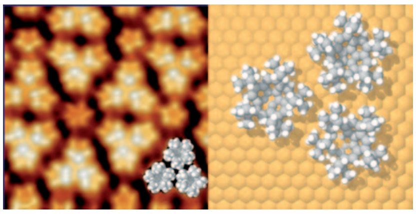


Corannulene Derivatives

O. Guillermet, E. Niemi, S. Nagarajan,
X. Bouju, D. Martrou, A. Gourdon,
S. Gauthier* ___ **1970 – 1973**

Self-Assembly of Fivefold-Symmetric Molecules on a Threefold-Symmetric Surface

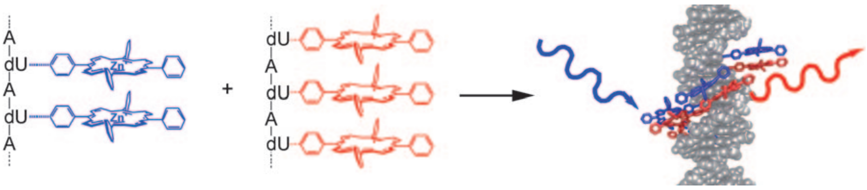
Buckybowls: The adsorption of penta-*tert*-butylcorannulene, a molecule with fivefold symmetry, on Cu(111), a surface with threefold symmetry, is investigated by scanning tunneling microscopy complemented by structure calculations. The symmetry mismatch is resolved by the formation of threefold-symmetric subunits consisting of three molecules, which combine with single molecules to form a nearly perfect filling of the plane (see picture).



DNA Structures

TN. Nguyen, A. Brewer,
E. Stulz* ___ **1974 – 1977**

Duplex Stabilization and Energy Transfer in Zipper Porphyrin–DNA

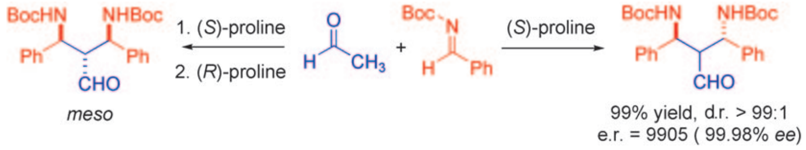


Zip it up: Attachment of porphyrins onto complementary DNA strands leads to zipper-porphyrin arrays and, in the presence of eleven modifications, an increase in the melting temperature of the duplex. Mixed zinc and free-base porphyrin arrays undergo energy transfer from the zinc porphyrin to the free-base porphyrin in the annealed duplex but not in the denatured form (see scheme), giving access to reversible formation of potential photonic wires.

Organocatalysis

C. Chandler, P. Galzerano, A. Michrowska, B. List* ______ 1978 – 1980

The Proline-Catalyzed Double Mannich Reaction of Acetaldehyde with *N*-Boc Imines



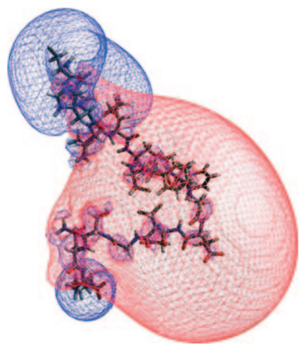
Double-cross: Proline catalyzes the double Mannich reaction of acetaldehyde with *N*-Boc imines in excellent yields (up to 99%; Boc = *tert*-butoxycarbonyl) and close to perfect diastereo- and enantioselectivities. Depending on the choice of catalysts, both the chiral, pseudo-C_2-symmetric diastereomer and the corresponding *meso* compound can be prepared. Cross double Mannich reactions of acetaldehyde with two different imines are also demonstrated.

Peptide–Peptide Interactions

A. Frydman-Marom, M. Rechter, I. Shefler, Y. Bram, D. E. Shalev, E. Gazit* ______ 1981 – 1986

Cognitive-Performance Recovery of Alzheimer's Disease Model Mice by Modulation of Early Soluble Amyloidal Assemblies

A rationally designed oligomerization inhibitor interacts with early intermediate assemblies of amyloid-β polypeptide (Aβ) through the aromatic elements and inhibits their assembly into the toxic oligomers that cause Alzheimer's disease by a unique C^{α}-methylation β-breakage strategy. The electrostatic potential of the low-energy conformation of the dipeptide inhibitor bound to Aβ is shown.

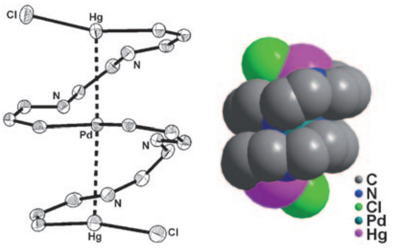


Metallamacrocycles

S. Sharma, R. S. Baligar, H. B. Singh,* R. J. Butcher ______ 1987 – 1990

Reaction of a Metallamacrocycle Leading to a Mercury(II)···Palladium(II)···Mercury(II) Interaction

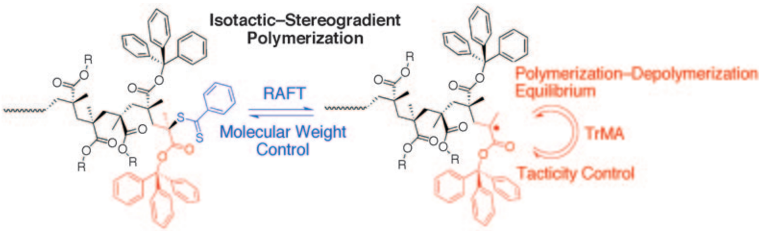
All wrapped up: The reaction of a 22-membered macrocycle derived from bis(*o*-formylphenyl)mercury and 1,2-phenylenediamine with palladium(II) results in cleavage of the macrocycle and concomitant formation of a trimetallic complex (see picture; phenyl rings truncated for clarity). The nature of the $Hg^{II}\cdots Pd^{II}\cdots Hg^{II}$ interaction was investigated by theoretical studies.



Polymerization

K. Ishitake, K. Satoh, M. Kamigaito,* Y. Okamoto ______ 1991 – 1994

Stereogradient Polymers Formed by Controlled/Living Radical Polymerization of Bulky Methacrylate Monomers

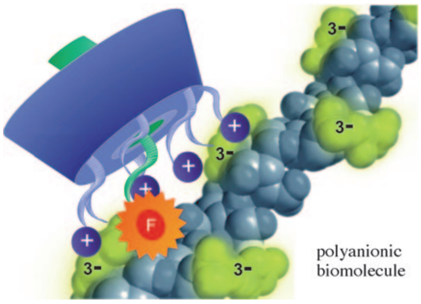


Life RAFT: A bulky methacrylate monomer, triphenylmethyl methacrylate (TrMA), was polymerized with reversible addition–fragmentation chain transfer (RAFT) agents. Stereogradient polymers in which the isospecificity increased spontaneously as the monomer concentration decreased were formed by a polymerization–depolymerization equilibrium that can convert a less stable growing polymer terminal into a more stable form (see picture).

Supramolecular Probes

R. B. C. Jagt, R. F. Gómez-Biagi,
M. Nitz* ________ **1995 – 1997**

Pattern-Based Recognition of Heparin Contaminants by an Array of Self-Assembling Fluorescent Receptors



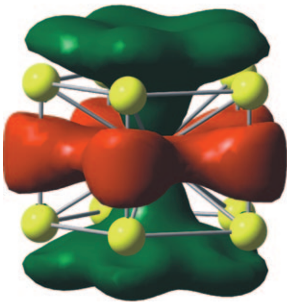
Tracking down potential killers: Strong host–guest interactions enable the facile combination of polycationic cyclodextrin binding motifs (blue) with fluorescent reporters (orange) tethered to a hydrophobic guest molecule (dark green). An array of supramolecular fluorescent receptors prepared by this modular approach was used for the pattern-based recognition of negatively charged contaminants in the anticoagulant drug heparin.

Cluster Compounds

J.-Q. Wang, S. Stegmaier,
T. F. Fässler* ________ **1998 – 2002**

$[Co@Ge_{10}]^{3-}$: An Intermetalloid Cluster with Archimedean Pentagonal Prismatic Structure

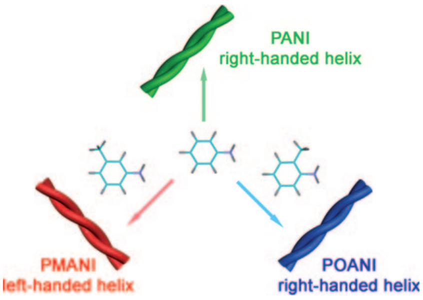
Inorganic pentaprismane: The unusual structure of the anion $[Co@Ge_{10}]^{3-}$, which was obtained by the reaction of K_4Ge_9 with $[Co(C_8H_{12})(C_8H_{13})]$ in ethylenediamine, raises questions about chemical bonding in the anion. The Zintl ion cluster has virtual D_{5h} symmetry and is a unique example of a ligand-free cluster that is not a deltahedron. The delocalized chemical bonding is represented in the picture by one of the bonding orbitals of the anion.



Chiral Polymers

Y. Yan, K. Deng, Z. Yu,
Z. Wei* ________ **2003 – 2006**

Tuning the Supramolecular Chirality of Polyaniline by Methyl Substitution

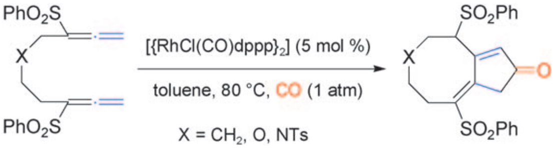


A game of Twister: The induced helicity of polyaniline and its supramolecular structures could be tuned by the methyl substitution of one of the monomers. By copolymerization of aniline with *m*-toluidine, the helicity of copolymer (PMANI) nanofibers was totally inverted compared to that of polyaniline (PANI), while copolymer nanofibers with *o*-toluidine (POANI) had the same helicity as that of polyaniline (see picture).

Cyclization

F. Inagaki, S. Narita, T. Hasegawa,
S. Kitagaki, C. Mukai* ________ **2007 – 2011**

Rhodium(I)-Catalyzed Intramolecular Carbonylative [2+2+1] Cycloaddition of Bis(allene)s: Bicyclo[6.3.0]undecadienones and Bicyclo[5.3.0]decadienones

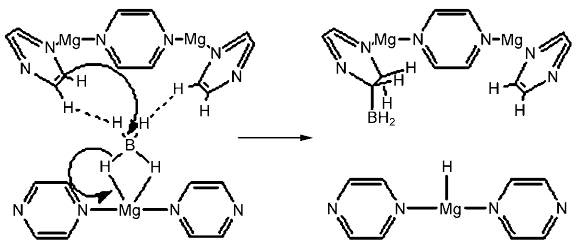


No templates needed: The title reaction makes it easy to construct the bicyclo[6.3.0]undecadienone framework in high yields (see scheme). A template effect is not required to achieve this ring-closing reaction efficiently. The present method can be applied to the construction of bicyclo[5.3.0] and bicyclo[4.3.0] ring systems. Ts = *p*-toluenesulfonyl.

Metal–Organic Frameworks

M. J. Ingleson, J. P. Barrio, J. Bacsa, A. Steiner, G. R. Darling, J. T. A. Jones, Y. Z. Khimyak, M. J. Rosseinsky* ______ **2012 – 2016**

Magnesium Borohydride Confined in a Metal–Organic Framework: A Preorganized System for Facile Arene Hydroboration

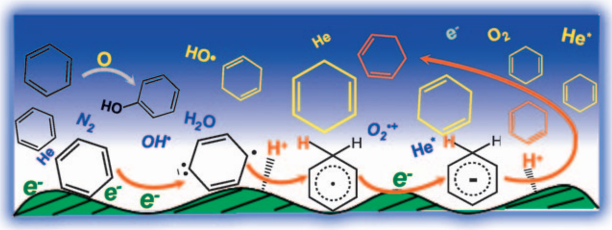


In close quarters: When confined in a metal–organic framework, magnesium borohydride reacts with arenes by a hydroboration pathway (see scheme), in contrast to its reactivity under analogous homogeneous solution-phase conditions. Framework-imposed organization of the reactive groups is required, which is achieved by a combination of the metal coordination and two hydrogen bonds.

Surface Reactions

N. Na, Y. Xia, Z. Zhu, X. Zhang,* R. G. Cooks* ______ **2017 – 2019**

Birch Reduction of Benzene in a Low-Temperature Plasma

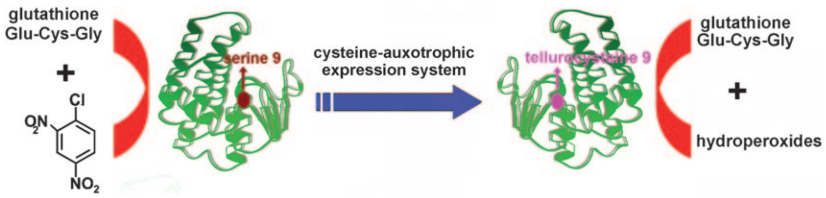


Selective and specific dihydrogenation of benzene and other arenes has been observed in a low-temperature helium plasma. A surface Birch reduction mechanism has been proposed in which benzene molecules adsorbed on the discharge surface capture low-energy surface-adsorbed electrons and subsequently undergo protonation (see picture). Gas-phase oxidation processes accompany the reduction reaction.

Enzyme Design

X. Liu, L. A. Silks, C. Liu, M. Ollivault-Shiflett, X. Huang, J. Li, G. Luo, Y.-M. Hou, J. Liu,* J. Shen ______ **2020 – 2023**

Incorporation of Tellurocysteine into Glutathione Transferase Generates High Glutathione Peroxidase Efficiency

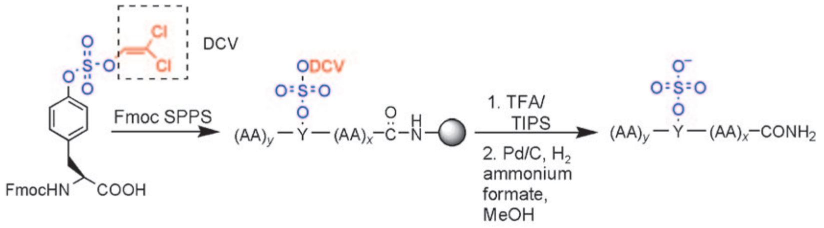


A rival to native peroxidase! An existing binding site for glutathione was combined with the catalytic residue tellurocysteine by using an auxotrophic expression system to create an engineered enzyme that functions as a glutathione peroxidase from the scaffold of a glutathione transferase (see picture). The catalytic activity of the telluroenzyme in the reduction of hydroperoxides by glutathione is comparable to that of native glutathione peroxidase.

Peptide Synthesis

A. M. Ali, S. D. Taylor* ______ **2024 – 2026**

Efficient Solid-Phase Synthesis of Sulfotyrosine Peptides using a Sulfate Protecting-Group Strategy



Double protection: Efficient Fmoc-based solid-phase synthesis (SPPS) of sulfotyrosine (sY) peptides is achieved by incorporating the sY residue(s) as a dichlorovinyl-protected (DCV) sulfodiester(s) and using 2-methylpiperidine for Fmoc removal. After removal of the other protecting groups, the DCV group could be cleaved by mild hydrogenolysis giving the sY peptides in good yield.

Gallium Chemistry (1)

Z. Zhu, X. Wang, M. M. Olmstead,
P. P. Power* ______ **2027 – 2030**

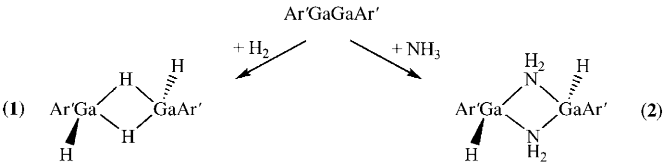
Synthesis and Characterization of $[Ar'GaC(Ph)CH]_2$ and $K_2[Ar'GaC(Ph)CH]_2\cdot OEt_2$: From Digallene to Digallacyclohexadiene to Digallatabenzene

On a plane: Addition of PhCCH to Ar′GaGaAr′ (Ar′ = 2,6-(2,6-$i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$) yielded the 1,4-digallacyclohexadiene $[\{Ar'GaC(Ph)CH\}_2]$ (**1**), which afforded the 1,4-digallatabenzene dianion $[Ar'GaC(Ph)CH]_2^{2-}$ (**2**) upon reduction with potassium (see scheme; C gray, Ga green, K blue). Structural parameters, DFT calculations, and ^{1}H NMR spectroscopy support aromatic character of **2**.

Gallium Chemistry (2)

Z. L. Zhu, X. Wang, Y. Peng, H. Lei,
J. C. Fettinger, E. Rivard,
P. P. Power* ______ **2031 – 2034**

Addition of Hydrogen or Ammonia to a Low-Valent Group 13 Metal Species at 25 °C and 1 Atmosphere



Mild-mannered: The low-valent aryl gallium(I) species :GaAr′ (Ar′ = 2,6-(2,6-$i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$) undergoes addition to H_2 or NH_3 at room temperature and one atmosphere of pressure to afford **1** or **2** (see scheme), which were characterized by X-ray crystallography and NMR and IR spectroscopy.

Hybrid Polyoxometalates

J. Li, I. Huth, L.-M. Chamoreau,
B. Hasenknopf,* E. Lacôte,*
S. Thorimbert,*
M. Malacria ______ **2035 – 2038**

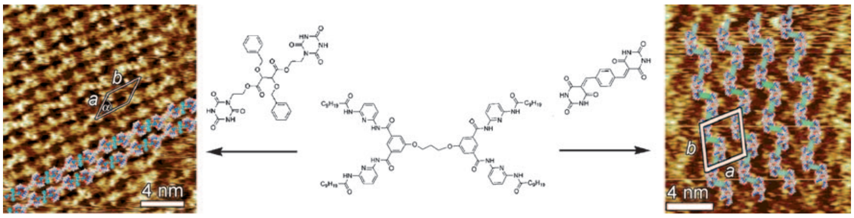
Insertion of Amides into a Polyoxometalate

POM alert: The incorporation of an amide oxygen atom into the framework of the Dawson-type polyoxometalate (POM) cluster $[P_2V_3W_{15}O_{62}]^{9-}$ (see picture) allows the communication of electronic effects between the organic and the inorganic parts of the molecule, including fine-tuning of the redox properties of the entire hybrid POM by the organic components, and transmission of the POM's electron-attracting properties to the organic moiety.

Supramolecular Polymers

A. Ciesielski, G. Schaeffer, A. Petitjean, J.-M. Lehn,* P. Samorì* ____ 2039 – 2043

STM Insight into Hydrogen-Bonded Bicomponent 1 D Supramolecular Polymers with Controlled Geometries at the Liquid–Solid Interface

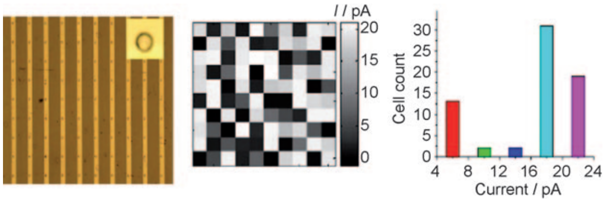


Bicomponent supramolecular polymers, consisting of two alternating molecules bridged through six H-bonds, are observed by STM at the solid–liquid interface. Control of the geometry of the 1D architecture was obtained by using two different connecting molecules with different conformational rigidity, affording either linear (see picture, left) or zigzag (right) motifs.

Single-Cell Analysis

Z. Lin, Y. Takahashi, T. Murata, M. Takeda, K. Ino, H. Shiku, T. Matsue* 2044 – 2046

Electrochemical Gene-Function Analysis for Single Cells with Addressable Microelectrode/Microwell Arrays

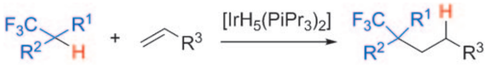


To each his own: An addressable electrochemical device consisting of orthogonally arranged rows and columns of electrodes has been constructed to monitor protein expression in genetically engineered cells at the single-cell level. The response based on redox cycling reflected the different expression levels of the enzyme from individual HeLa cells transfected with a plasmid vector including secreted alkaline phosphatase.

C–H Activation

Y. Guo, X. Zhao, D. Zhang, S.-I. Murahashi* ________ 2047 – 2049

Iridium-Catalyzed Reactions of Trifluoromethylated Compounds with Alkenes: A C_{sp^3}–H Bond Activation α to the Trifluoromethyl Group



Catalytic convenience: The use of iridium or ruthenium catalysts for C_{sp^3}–H bond activation has led to the addition reaction of trifluoromethylated compounds to alkenes (see scheme). This atom-economical reaction occurs under neutral reaction conditions and without the formation of undesired defluorinated by-products, even at high temperature.

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

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

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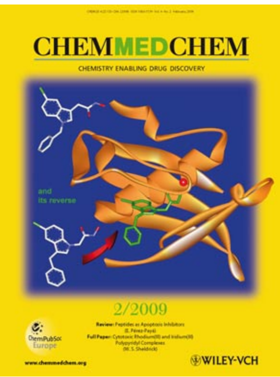

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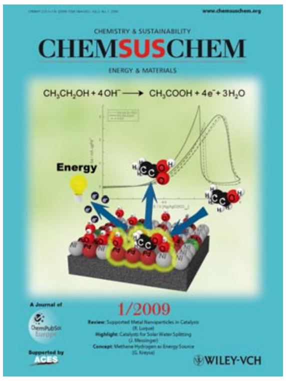

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