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:*

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*A. B. Chaplin, A. S. Weller**
B–H Activation at a Rhodium(I) Center: A Missing Link in the Transition-Metal-Catalyzed Dehydrocoupling of Amine–Boranes

*G. de Ruiter, E. Tartakovsky, N. Oded, M. E. van der Boom**
Sequential Logic Operations with Surface-Confined Polypyridyl Complexes Having Molecular Random Access Memory Features

*W. Li, P. H. C. Camargo, L. Au, Q. Zhang, M. Rycenga, Y. Xia**
Etching and Dimerization: A Simple and Versatile Route to Dimers of Silver Nanospheres with a Range of Sizes

*I. U. Khan, D. Zwanziger, I. Böhme, M. Javed, H. Naseer, S. W. Hyder, A. G. Beck-Sickinger**
Breast Cancer Diagnosis by Neuropeptide Y Analogues: From Synthesis to Clinical Application

*K. Fesko, M. Uhl, J. Steinreiber, K. Gruber, H. Griengl**
Biocatalytic Access to α,α-Dialkyl-α-amino Acids by a Mechanism-Based Approach

*T. Yokoi, M. Yoshioka, H. Imai, T. Tatsumi**
Diversification of RTH-type Zeolite and Its Catalytic Application

Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, W.-S. Yang, J. Caro**
Metal–Organic Framework Molecular Sieve Membrane: Supported ZIF-7 Layer with High Hydrogen Selectivity by Microwave-Assisted Seeded Growth

Author Profile

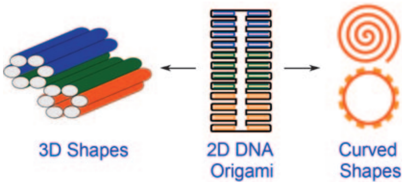
"If I could be anyone for a day, I would be the conductor of a symphonic orchestra.
When I was eighteen I wanted to be a teacher. …"
This and more about Gérard Férey can be found on page 9398.

Obituary

Books

Highlights

DNA Nanotechnology

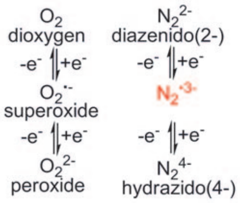


DNA folding as an extended art form: Long strands of DNA can be folded in a controlled manner to yield 3D shapes. Moreover, twisted and curved shapes can be created with excellent control (see schematic representation). The key to these developments is the use of Holliday junctions, which connect different parts of the array and also create tension in the honeycomb system so that the DNA structure is forced to fold into the desired shape.

Nitrogen Radicals

W. Kaim,* B. Sarkar* ______ **9409 – 9411**

$N_2^{\bullet 3-}$: Filling a Gap in the N_2^{n-} Series



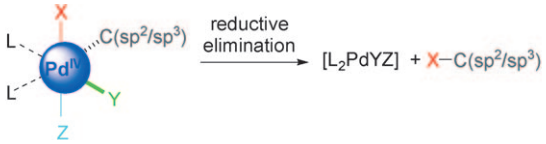
The unexpected stability of the exotic $N_2^{\bullet 3-}$ species has been observed in complexes with Dy^{3+} and Y^{3+}. The three-electron reduction product of N_2 is isoelectronic with superoxide $O_2^{\bullet -}$ (see scheme) and is a possible bound intermediate in the conversion of N_2 into NH_3.

Minireviews

Palladium(IV) Catalysis

K. Muñiz* ______ **9412 – 9423**

High-Oxidation-State Palladium Catalysis: New Reactivity for Organic Synthesis



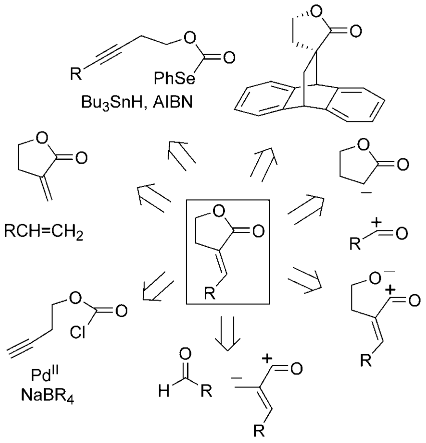
The higher, the better! The emergence in recent years of catalysis with high-oxidation-state palladium complexes has enabled the functionalization of alkyl and aryl compounds in a series of new reactions (see general scheme). Reaction processes and mechanistic aspects of these catalytic transformations are discussed in this Minireview.

Reviews

Butyrolactones

R. R. A. Kitson, A. Millemaggi,
R. J. K. Taylor* ______ **9426 – 9451**

The Renaissance of α-Methylene-γ-butyrolactones: New Synthetic Approaches



Flower power: The structures, biological activities, and biosynthesis of α-methylene-γ-butyrolactone and α-alkylidene-γ-butyrolactone natural products—which are found, for example, in arnica, feverfew, and, peony—are reviewed, as are recent synthetic approaches.

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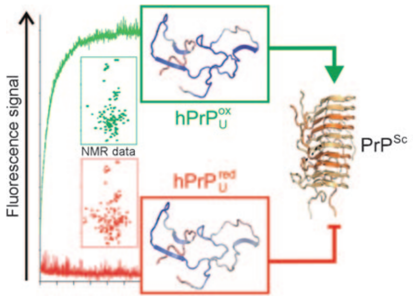
Communications

Protein Structures

C. Gerum, R. Silvers,
J. Wirmer-Bartoschek,
H. Schwalbe* ______ 9452 – 9456

Unfolded-State Structure and Dynamics Influence the Fibril Formation of Human Prion Protein

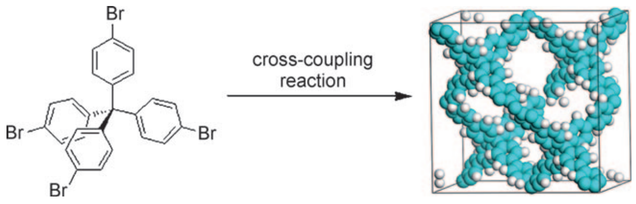


Rigid bridges: NMR studies of the unfolded state (U) of the human prion protein (PrP) show that in the oxidized form the native disulfide bridge between two cysteine residues rigidifies the surrounding amino acids. This area is a hotspot region of the protein in terms of disease-related mutations that promote aggregation and formation of the abnormal “scrapie” form (PrP^{Sc}).

Porous Organic Frameworks

T. Ben, H. Ren, S. Ma, D.-P. Cao, J.-H. Lan,
X.-F. Jing, W.-C. Wang, J. Xu, F. Deng,
J. M. Simmons, S.-L. Qiu,*
G. S. Zhu* ______ 9457 – 9460

Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area

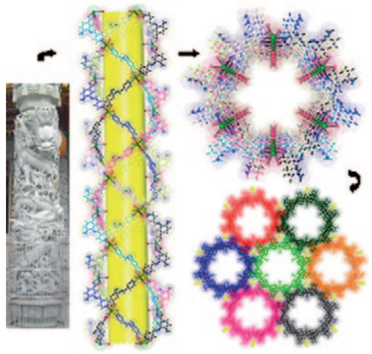


Diamonds are forever: A diamond-like framework in which the C–C bonds are replaced with rigid phenyl rings (see picture) is not only structurally stable but also has a large internal surface area. This porous aromatic framework (PAF-1) demonstrates high uptake capacities of hydrogen and carbon dioxide as well as benzene and toluene vapors, and has an unprecedented surface area of 7100 m^2 g^{-1}.

Metal–Organic Nanotubes

T.-T. Luo, H.-C. Wu, Y.-C. Jao, S.-M. Huang,
T.-W. Tseng, Y.-S. Wen, G.-H. Lee,
S.-M. Peng, K.-L. Lu* ______ 9461 – 9464

Self-Assembled Arrays of Single-Walled Metal–Organic Nanotubes

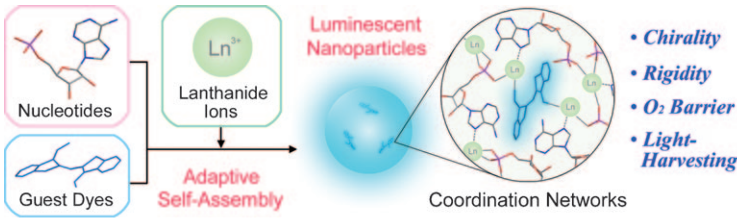


Dragon’s lair: A large, single-walled metal–organic nanotube (MONT) with an exterior diameter of up to 3.2 nm and an internal channel diameter of 1.4 nm is presented. The tube can be depicted as hexastranded helices consisting of three right-handed and three left-handed helical chains, and resembles a rolled-up dragon column (see picture). The MONTs are held together by alkaline ions to form unique nanotubular arrays.

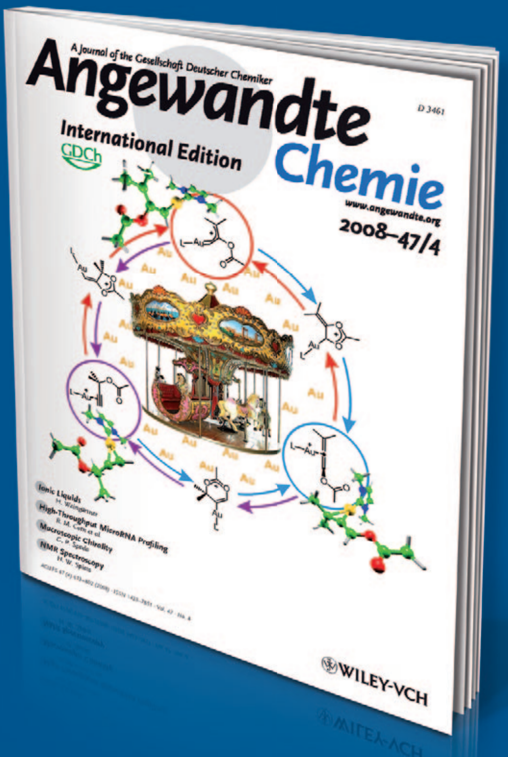
Self-Assembly

R. Nishiyabu, C. Aimé, R. Gondo,
T. Noguchi, N. Kimizuka* ______ 9465 – 9468

Confining Molecules within Aqueous Coordination Nanoparticles by Adaptive Molecular Self-Assembly



Dying on the inside: Functional dye molecules can be adaptively encapsulated in coordination nanoparticles (CNPs) of nucleotides and lanthanide ions in the course of their formation in water (see picture). Dyes confined in CNPs are conformationally restricted and surprisingly stable against molecular oxygen. These properties should be favorable for the development of light-harvesting CNPs.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2008–47/4
WILEY-VCH

Prion Misfolding

J. C. Scheinost, D. P. Witter, G. E. Boldt,
J. Offer, P. Wentworth, Jr.* ____ **9469–9472**

Cholesterol Secosterol Adduction Inhibits the Misfolding of a Mutant Prion Protein Fragment that Induces Neurodegeneration

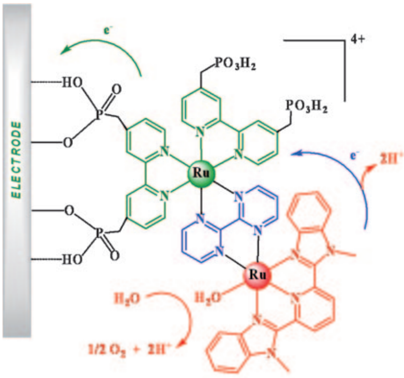
Aldehyde is critical: Atheronal-B, a cholesterol secosterol aldehyde (see structure), completely inhibits the misfolding of a prion protein fragment from its α to β form through a mechanism that involves adduction to the protein. This result offers a fresh view of lipid aldehyde-induced protein misfolding and provides a promising molecular scaffold on which to develop potential prion disease therapeutics.

Water Oxidation

J. J. Concepcion, J. W. Jurss, P. G. Hoertz,
T. J. Meyer* ____ **9473–9476**

Catalytic and Surface-Electrocatalytic Water Oxidation by Redox Mediator–Catalyst Assemblies

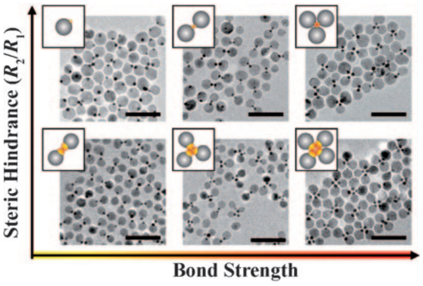
All-in-one assemblies containing single-site water oxidation catalysts (red and blue) and redox mediators (green and blue) act as stable, robust catalysts toward water oxidation, both in solution and anchored to metal oxide surfaces by phosphonate linkers on the mediator. More than 28000 turnovers have been achieved with > 95% Faradaic efficiency for oxygen production without reduced catalytic activity.



Nanoparticles

Y. Wei, K. J. M. Bishop, J. Kim, S. Soh,
B. A. Grzybowski* ____ **9477–9480**

Making Use of Bond Strength and Steric Hindrance in Nanoscale “Synthesis”

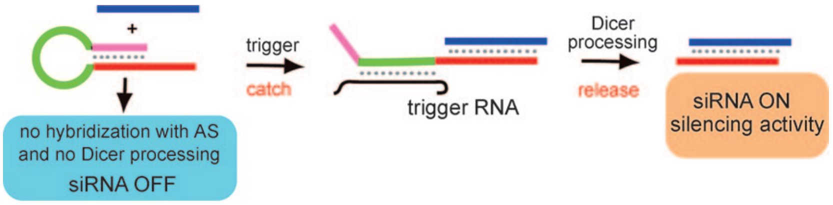


The chemical concepts of bond strength and steric hindrance are extended to the nanoscale to control “reactions” of composite nanoparticles into primitive “nanomolecules” of well-defined shapes and sizes. The progress of these nanoscale transformations is controlled by an interplay between the strength of bonding between particles’ reactive domains and the entropic effects because of the bulkiness of the unreactive parts.

RNA Probes

H. Masu, A. Narita, T. Tokunaga,
M. Ohashi, Y. Aoyama,*
S. Sando* ____ **9481–9483**

An Activatable siRNA Probe: Trigger-RNA-Dependent Activation of RNAi Function

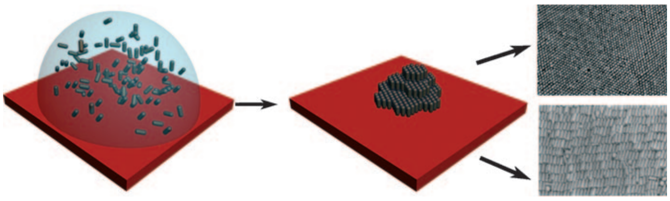


Catch and release: A hairpin-shaped sense strand (red)/antisense strand (blue) siRNA probe was designed to be activated by a trigger RNA molecule. In the presence of the trigger RNA, clear OFF-to-ON switching of RNAi activity was observed with high sequence dependency (see schematic illustration).

Nanorod Assembly

A. Guerrero-Martínez,* J. Pérez-Juste,
E. Carbó-Argibay, G. Tardajos,
L. M. Liz-Marzán* ———— **9484 – 9488**

Gemini-Surfactant-Directed Self-Assembly of Monodisperse Gold Nanorods into Standing Superlattices



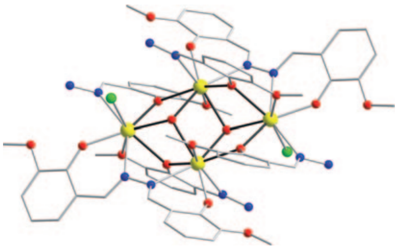
A super lattice: The title system allows the spontaneous formation of self-assembled 2D and 3D highly ordered aggregates of standing nanorods on large superlattice domains (see picture). The hexagonal close packing of nanorods perpendicular to the substrate resembles smectic-B liquid-crystalline phases. Optical characterization of the aggregates demonstrates their anisotropic optical response.

Single-Molecule Magnets

P.-H. Lin, T. J. Burchell, L. Ungur,
L. F. Chibotaru, W. Wernsdorfer,
M. Murugesu* ———— **9489 – 9492**

A Polynuclear Lanthanide Single-Molecule Magnet with a Record Anisotropic Barrier

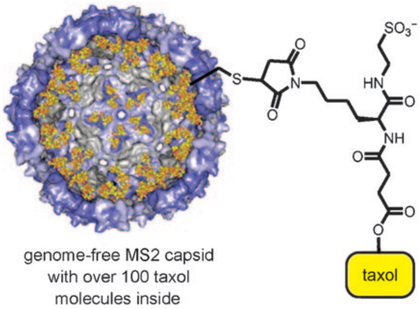
Magnetic measurements on a $\{Dy_4\}$ single-molecule magnet (SMM) with a defect-dicubane central core, synthesized using 1,2-bis(2-hydroxy-3-methoxybenzylidene) hydrazone and 3-methoxysalicylaldehyde hydrazone as chelating agents (see structure; yellow Dy, red O, blue N, green Cl), confirm SMM behavior and reveal hysteresis loops at 7 K. The anisotropic energy barrier of $U_{eff} = 170$ K is the highest reported to date.



Drug Delivery

W. Wu, S. C. Hsiao, Z. M. Carrico,
M. B. Francis* ———— **9493 – 9497**

Genome-Free Viral Capsids as Multivalent Carriers for Taxol Delivery

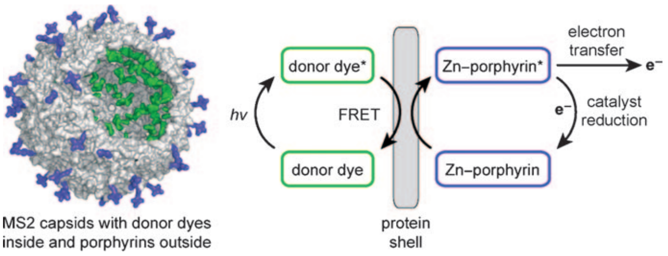


Delivery by Trojan horse: A water-soluble derivative of the chemotherapeutic agent taxol was synthesized with bioconjugation functionality and attached to capsids of the bacteriophage MS2 (see picture). The modified capsids retained their form and released taxol when incubated with MCF-7 cells. The resulting cell-viability levels were similar to those observed upon treatment with free taxol in solution.

Energy Transfer

N. Stephanopoulos, Z. M. Carrico,
M. B. Francis* ———— **9498 – 9502**

Nanoscale Integration of Sensitizing Chromophores and Porphyrins with Bacteriophage MS2

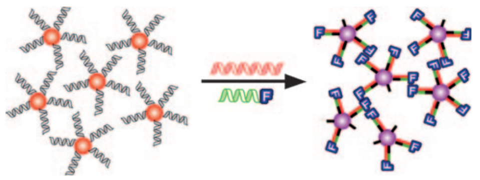


Harnessing energy from within: Energy transfer from the inside to the outside of MS2 capsids modified by positioning fluorescent dyes and a photocatalytic zinc porphyrin on their surfaces (see picture) enabled sensitization of the porphyrin at multiple wavelengths and thus broad-spectrum catalytic activity.

DNA Detection

M. Hong, X. Zhou, Z. Lu,
J. Zhu* 9503 – 9506

Nanoparticle-Based, Fluorous-Tag-Driven DNA Detection



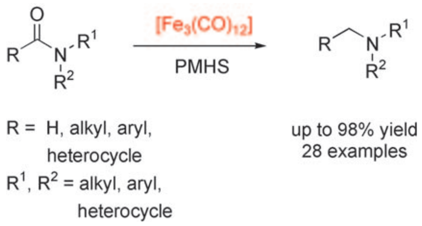
Tagging along: A DNA detection method has been developed that relies on the interfacial assembly of gold nanoparticles. The fluorous-tag-driven formation of nanoparticle networks (see scheme) at the gas/liquid, liquid/liquid, or solid/liquid interface is such that a single type of assembly architecture is suitable for an array of detection formats.

Homogeneous Catalysis

S. Zhou, K. Junge, D. Addis, S. Das,
M. Beller* 9507 – 9510

A Convenient and General Iron-Catalyzed Reduction of Amides to Amines

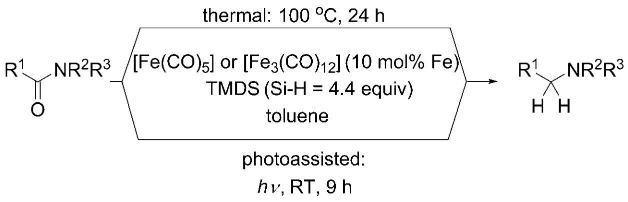
While the iron is hot: The first general and efficient iron-catalyzed reduction of secondary and tertiary amides into amines using polymethylhydrosiloxane (PMHS) has been developed (see scheme).



Iron-Catalyzed Reduction

Y. Sunada, H. Kawakami, T. Imaoka,
Y. Motoyama,
H. Nagashima* 9511 – 9514

Hydrosilane Reduction of Tertiary Carboxamides by Iron Carbonyl Catalysts

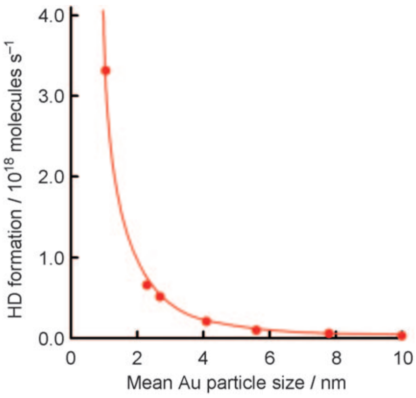


Fox in the carboxamide: Reduction of tertiary carboxamides to their corresponding amines is catalyzed by $[Fe(CO)_5]$ or $[Fe_3(CO)_{12}]$, using 1,1,3,3-tetramethyldisiloxane (TMDS) as the reducing agent. The reaction proceeds under either thermal or photochemical conditions. Unlike the hydrosilane reduction of amides using platinum or ruthenium catalysts, TMDS preferentially reduces a nitro group, even in the presence of competing amides.

Heterogeneous Catalysis

T. Fujitani,* I. Nakamura, T. Akita,
M. Okumura, M. Haruta 9515 – 9518

Hydrogen Dissociation by Gold Clusters



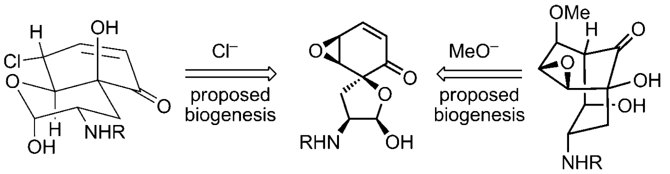
The rate of H_2–D_2 exchange increases in proportion to the inverse square of the mean diameter of gold particles supported on TiO_2 (see picture), which indicates that hydrogen dissociation takes place on the perimeter interfaces between the gold and TiO_2 and that the catalytic activity for H_2 dissociation is correlated neither to a change in the fraction of edge or corner sites nor to a change in the electronic nature induced by the quantum size effect.

Contents

Biomimetic Synthesis

J. Y. Cha, Y. Huang,
T. R. R. Pettus* ———— **9519–9521**

Total Synthesis of TK-57-164A, Isariotin F, and Their Putative Progenitor Isariotin E



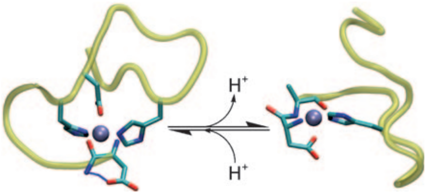
isariotin F (**2**) isariotin E (**3**) TK-57-164A (**1**)

Keeping it simple: A simple strategy for the total synthesis of three complex natural products has been developed, while also confirming the putative generation of **1** and **2** from **3**. The benefits of a simple dissymmetric 2,5-cyclohexadienone are illustrated and provide the foundation for rapid diastereoselective functionalization leading to the first total synthesis of these compounds.

Peptide Binding

C. Hureau,* Y. Coppel, P. Dorlet,
P. L. Solari, S. Sayen, E. Guillon,
L. Sabater, P. Faller* ———— **9522–9525**

Deprotonation of the Asp1–Ala2 Peptide Bond Induces Modification of the Dynamic Copper(II) Environment in the Amyloid-β Peptide near Physiological pH

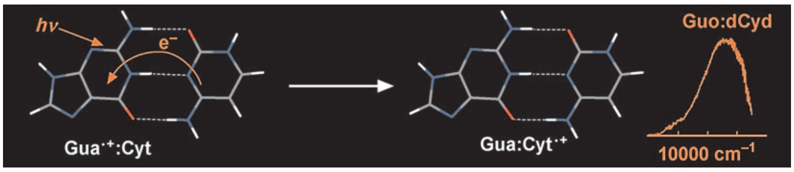


Premium bonds: The pH-dependent coordination of $\mathrm{Cu^{II}}$ to the Alzheimer's disease amyloid-β peptide has been studied by NMR spectroscopy. Several equivalent ligands are in equilibrium for $\mathrm{Cu^{II}}$ binding near pH 6.6 and 8.7. Fewer conformers are detected at high pH, in line with a reshuffling of the $\mathrm{Cu^{II}}$ binding site induced by deprotonation of the Asp1–Ala2 peptide bond (see picture).

Nucleoside Complexes

A. Capobianco, M. Carotenuto, T. Caruso,
A. Peluso* ———— **9526–9528**

The Charge-Transfer Band of an Oxidized Watson–Crick Guanosine–Cytidine Complex



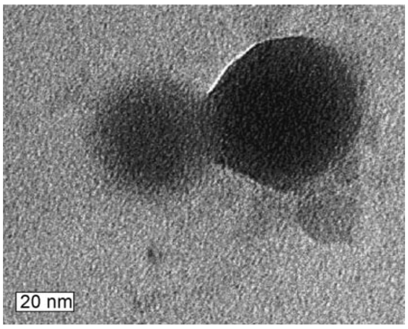
The hole truth: A low-energy band in the absorption spectrum of the oxidized Watson–Crick complex of guanosine and cytidine derivatives (see scheme) is attributed to charge-transfer localizing the hole from one-electron oxidation on the cytidine moiety. The band provides an estimate of the energy of one of the low-lying electronic states of oxidized duplex DNA.

Sonochemistry

S. I. Nikitenko,* P. Martinez, T. Chave,*
I. Billy ———— **9529–9532**

Sonochemical Disproportionation of Carbon Monoxide in Water: Evidence for Treanor Effect during Multibubble Cavitation

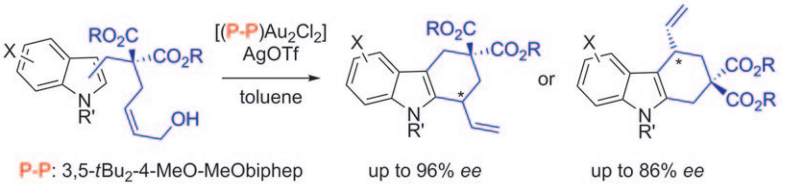
A sound reaction: The ultrasonically driven disproportionation of CO in water causes formation of hydrated polymer of carbon suboxide $(C_3O_2)_n$ (see picture) enriched with a heavy ^{13}C isotope. This finding indicates the presence of vibrationally excited CO molecules with a non-equilibrium Treanor distribution inside the cavitating bubble.



Alkylation

M. Bandini,* A. Eichholzer — **9533 – 9537**

Enantioselective Gold-Catalyzed Allylic Alkylation of Indoles with Alcohols: An Efficient Route to Functionalized Tetrahydrocarbazoles

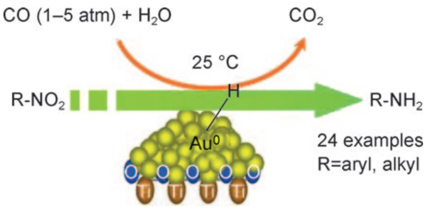


Breaking the taboo: The direct use of allylic alcohols in catalytic and enantioselective Friedel–Crafts alkylation is described for the first time in the presence of chiral gold complexes. This intramolecular Friedel–Crafts reaction was used to prepare a broad range of functionalized tetrahydrocarbazoles (see scheme; X = Me, F, Br, Cl, OMe; R = Me, Et, *t*Bu; R′ = H, Me).

Sustainable Gold Catalysis

L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao,* H. Y. He, K. N. Fan ——— **9538 – 9541**

Efficient and Selective Room-Temperature Gold-Catalyzed Reduction of Nitro Compounds with CO and H_2O as the Hydrogen Source

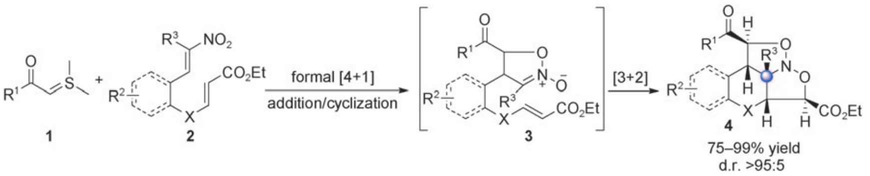


Taking hydrogen from water: Gold catalysis enabled the selective reduction of nitro compounds under very mild conditions with a combination of H_2O and CO as the reductant (see scheme). This environmentally friendly reaction proceeded in high yield and with high chemoselectivity in the presence of a wide range of functional groups.

Cascade Reaction

L.-Q. Lu, F. Li, J. An, J.-J. Zhang, X.-L. An, Q.-L. Hua, W.-J. Xiao* ——— **9542 – 9545**

Construction of Fused Heterocyclic Architectures by Formal [4+1]/[3+2] Cycloaddition Cascade of Sulfur Ylides and Nitroolefins



Under control: A formal [4+1]/[3+2] cycloaddition cascade of sulfur ylides and alkene-tethered nitroolefins has been developed, and provides an efficient synthesis of fused polycyclic heterocyclic compounds in good to excellent overall yields with excellent diastereocontrol (see scheme). A catalytic asymmetric variant of this reaction has also been disclosed.

Enzymatic Synthesis

H. Stecher, M. Tengg, B. J. Ueberbacher, P. Remler, H. Schwab, H. Griengl, M. Gruber-Khadjawi* ——— **9546 – 9548**

Biocatalytic Friedel–Crafts Alkylation Using Non-natural Cofactors

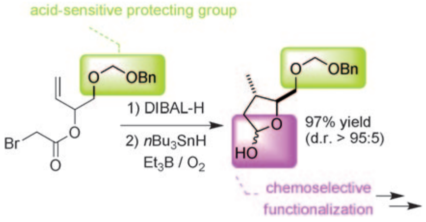
A novel biocatalytic protocol for C–C bond formation is described and is an equivalent to Friedel–Crafts alkylation. *S*-Adenosyl-L-methionine (SAM), the major methyl donor for biological methylation catalyzed by methyltransferases (Mtases), can perform alkylations (see scheme). These enzymes can accept non-natural cofactors and transfer functionalities other than methyl onto aromatic substrates.

Radical Reactions

A. Boussonnière, F. Dénès,*
J. Lebreton* ______________ **9549 – 9552**

Radical Cyclization of α-Bromo Aluminum Acetals: An Easy Approach to γ-Lactols

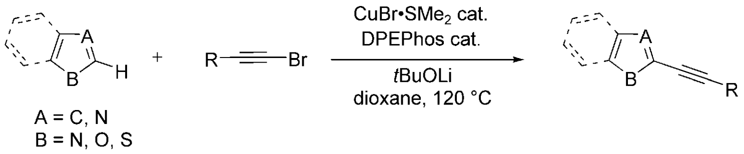
Running rings around aluminum: An efficient procedure for radical cyclization of α-bromo esters is reported. Reduction of the esters by DIBAL-H at low temperature gives aluminum acetals, which are cyclized in the presence of $n\mathrm{Bu_3SnH}$ and $\mathrm{Et_3B}$ (see scheme). These one-pot conditions lead to polysubstituted γ-lactols in high yields, and the mildness of the reaction conditions allows the preparation of acid-sensitive derivatives.



C–H Bond Activation

F. Besselièvre, S. Piguel* ___ **9553 – 9556**

Copper as a Powerful Catalyst in the Direct Alkynylation of Azoles

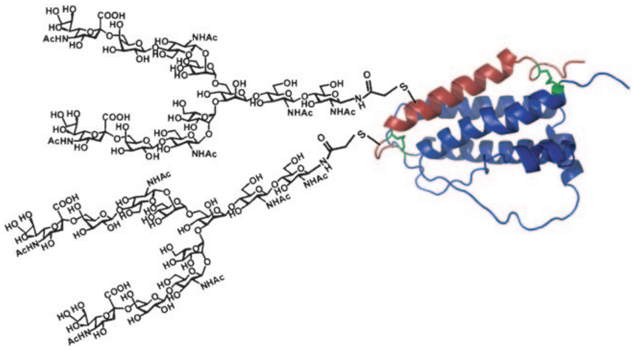


Copper-bottomed catalysis! The direct alkynylation of azoles through a copper-based C–H bond activation, using alkynylbromides as the coupling partner, has been developed (see scheme). The method is very rapid, is functional-group tolerant, and provides a straightforward entry to diverse alkynyl heterocycles that is complementary to the Sonogashira reaction.

Glycoprotein Synthesis

K. Hirano, D. Macmillan, K. Tezuka,
T. Tsuji, Y. Kajihara* ________ **9557 – 9560**

Design and Synthesis of a Homogeneous Erythropoietin Analogue with Two Human Complex-Type Sialyloligosaccharides: Combined Use of Chemical and Bacterial Protein Expression Methods



Highly expressive: Cell proliferation was observed with concentrations of an erythropoietin (EPO) analogue above 50 pg mL^{-1}. The EPO analogue has two human complex-type sialyloligosaccharides (see picture) and was formed by the combined use of chemical synthesis and protein expression in *E. coli*. Both the 24- and 30-positions are glycosylated, but the two sialyloligosaccharides do not interfere with binding of the EPO analogue to a receptor.

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

Corrigendum

In this Communication entry 16 in Table 3 shows the wrong substrate and the wrong product: 4-bromoacetophenone as the substrate and 4-hydroxyacetophenone as the product should be replaced by 4-bromobenzophenone and 4-hydroxybenzophenone, respectively.

Palladium-Catalyzed Hydroxylation of Aryl Halides under Ambient Conditions

A. G. Sergeev, T. Schulz, C. Torborg, A. Spannenberg, H. Neumann, M. Beller* ______ **7595–7599**

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