The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

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

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

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

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

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

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

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

*R. Volinsky, R. Jelinek**
Laser-Modulated Ordering of Au Nanoparticles at the Air/Water Interface

*X. Zeng, H. Beckers, H. Willner**
Difluoro-λ^5-Phosphinonitrile $F_2P{=}N$: Matrix Isolation and Photoisomerization into $FP{=}NF$

*H. Huang, B. Chung, J. Jung, H.-W. Park, T. Chang**
Toroidal Micelles of Uniform Size from Diblock Copolymers

*R. Koller, K. Stanek, D. Stolz, R. Aardoom, K. Niedermann, A. Togni**
Zn-Mediated Formation of Trifluoromethyl Ethers From Alcohols Using Hypervalent Iodine Trifluoromethylation Reagents

Author Profile

"The secret of being a successful scientist is to devote oneself to one thing.
The biggest challenge facing scientists is to recruit young talented students who are willing to enjoy ventures in science. …"
This and more about Wonwoo Nam can be found on page 4100.

News

J. P. Collman

K. D. Karlin

D. A. King

Contents

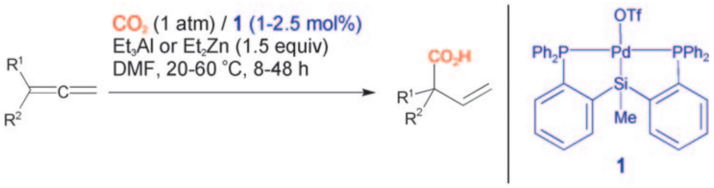
Books

Highlights

Hydrocarboxylation

M. North* ______ **4104–4105**

Synthesis of β,γ-Unsaturated Acids from Allenes and Carbon Dioxide



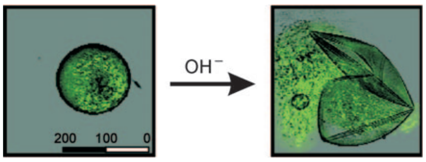
Hidden talent: Often perceived to be too thermodynamically and kinetically inert to be a useful chemical feedstock, carbon dioxide adds to allenes under exceptionally mild reductive conditions in the presence of a palladium pincer complex to give β,γ-unsaturated carboxylic acids (see scheme). This transformation is discussed in the context of the requirements for CO_2 fixation. DMF = *N*,*N*-dimethylformamide, Tf = trifluoromethanesulfonyl.

Nanoparticle Bombs

L. Dähne* ______ **4106–4108**

Nanoparticle Missiles from Exploding Polyelectrolyte Capsules

Out with a bang! Microcapsules have been prepared which, as a result of an explosion triggered by an external stimulus, distribute nanoparticles throughout the local environment both efficiently and rapidly (see picture). In this way a principle found in nature for the dispersal of seeds and defensive materials has now been realized in nanotechnology and might be utilized, for example, for the better distribution of drugs in organs.

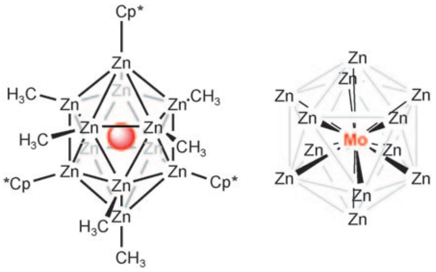


Cluster Compounds

D. L. Kays,* S. Aldridge* ______ **4109–4111**

Bridging the Gap between Coordination and Cluster Compounds: Unusual Bonding Modes for Zinc

Inner virtue: The reaction of $[Mo^0(GaCp^*)_6]$ with $ZnMe_2$ yields the novel multinuclear zinc system $[MoZn_{12}Me_9Cp^*_3]$ which geometrically resembles a classical Wade–Mingos cluster (with an interstitial molybdenum atom, see picture). In reality, its electronic structure features little direct Zn–Zn bonding, relying instead on Mo–Zn three-center, two-electron bonds spanning the body diagonals of the approximately icosahedral framework.



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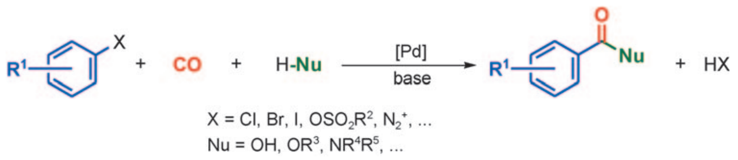
Reviews

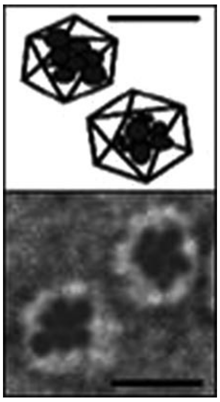
Palladium Catalysis



A CO group richer: (Hetero)arenes are vital intermediates in the manufacture of agrochemicals, dyes, pharmaceuticals, and other industrial products. In the past decades transition-metal-catalyzed coupling reactions of aryl halides with all types of nucleophiles have been developed. This Review summarizes recent work in the area of palladium-catalyzed carbonylation reactions of aryl halides and related compounds (see scheme).

Communications

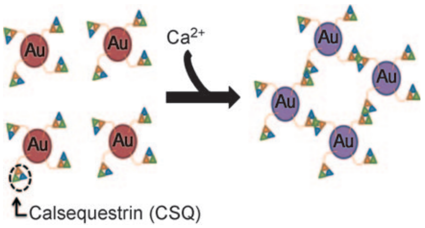
DNA Nanotechnology

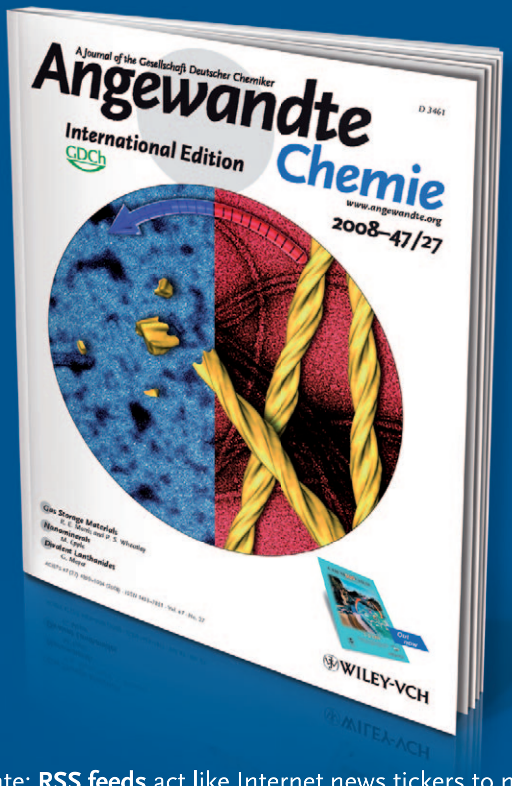


It's a trap! DNA polyhedra formed through molecular self-assembly may function as nanocapsules for the targeted delivery of encapsulated entities. This functional aspect was demonstrated for the most complex DNA-based platonic solid: During the stepwise amalgamation of discrete polyhedra to form icosahedra, gold nanoparticles (GNPs) were encapsulated from solution (see illustration and TEM image of icosahedral cages containing GNPs).

Calcium Sensors

Seeing is sensing: Calsequestrin (CSQ) functionalized gold nanoparticles undergo calcium-dependent CSQ polymerization, which results in a clear color change (see picture) together with precipitation. The sensing system is specific for Ca^{2+} ions and the differences between normal and disease-associated abnormal (hypercalcemia) Ca^{2+} ion levels in serum can be distinguished with the naked eye.

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Angewandte Chemie
International Edition
GDCh
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2008–47/27
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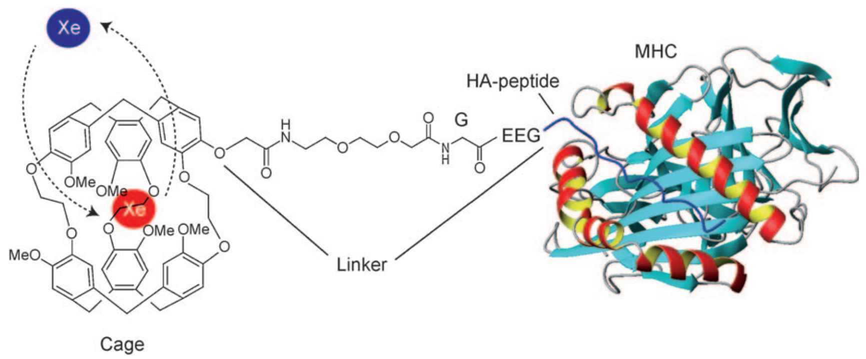
Molecular Targeting

A. Schlundt, W. Kilian, M. Beyermann, J. Sticht, S. Günther, S. Höpner, K. Falk, O. Roetzschke, L. Mitschang, C. Freund* ______ **4142 – 4145**

A Xenon-129 Biosensor for Monitoring MHC–Peptide Interactions

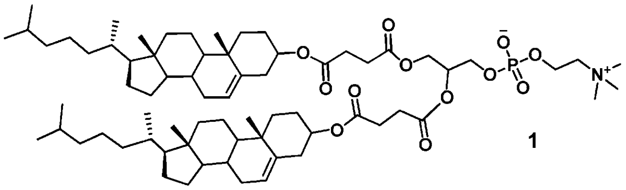


Caged in: The formation of a complex between a peptide ligand and a major histocompatibility complex (MHC) class II protein is detected by a ^{129}Xe biosensor. Cryptophane molecules that trap Xe atoms are modified with a hemagglutinin (HA) peptide, which binds to the MHC protein. The interaction can be monitored by an NMR chemical shift change of cage–HA bound ^{129}Xe.

Drug Nanocarriers

Z. Huang, M. R. Jaafari, F. C. Szoka, Jr.* ______ **4146 – 4149**

Disterolphospholipids: Nonexchangeable Lipids and Their Application to Liposomal Drug Delivery

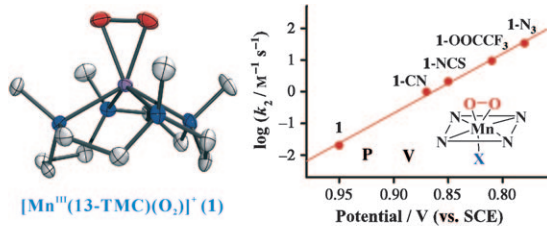


Extreme makeover of cholesterol: Cholesterol exchange is a major reason for the instability of liposomes in blood. The formation of a covalent hybrid between cholesterol and glycerophosphocholine preserves the bilayer-stabilizing effect of free cholesterol but prevents its transfer from the bilayer. Thus, disterolphospholipids (e.g. **1**) are valuable new components for liposome formulation.

Enzyme Models

J. Annaraj, J. Cho, Y.-M. Lee, S. Y. Kim, R. Latifi, S. P. de Visser,* W. Nam* ______ **4150 – 4153**

Structural Characterization and Remarkable Axial Ligand Effect on the Nucleophilic Reactivity of a Nonheme Manganese(III)–Peroxo Complex



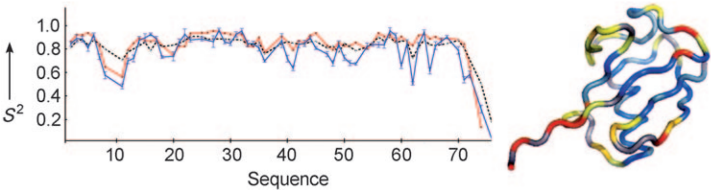
The dark side of the Mn: A manganese(III) complex bearing a 13-membered macrocyclic ligand (**1**, see picture) binds a peroxo ligand in a side-on η^2 fashion. The reactivity of **1** is influenced by the introduction of anionic ligands *trans* to the peroxo group. Electronic and structural changes upon *trans*-ligand binding explain the increased nucleophilicity of the resulting complexes **1**-X.

Contents

Protein Dynamics

L. Salmon, G. Bouvignies, P. Markwick, N. Lakomek, S. Showalter, D. W. Li, K. Walter, C. Griesinger, R. Brüschweiler, M. Blackledge* ______ **4154 – 4157**

Protein Conformational Flexibility from Structure-Free Analysis of NMR Dipolar Couplings: Quantitative and Absolute Determination of Backbone Motion in Ubiquitin

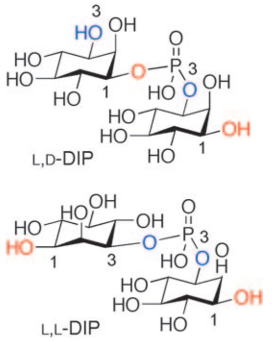


A robust procedure for the determination of protein-backbone motions on time scales of pico- to milliseconds directly from residual dipolar couplings has been developed that requires no additional scaling relative to external references. The results for ubiquitin (blue in graph: experimental N−HN order parameters) correspond closely to the amplitude, nature, and distribution of motion found in a 400 ns molecular-dynamics trajectory of ubiquitin (red).

Asymmetric Catalysis

C. M. Longo, Y. Wei, M. F. Roberts, S. J. Miller* ______ **4158 – 4161**

Asymmetric Syntheses of L,L- and L,D-Di-*myo*-inositol-1,1′-phosphate and their Behavior as Stabilizers of Enzyme Activity at Extreme Temperatures



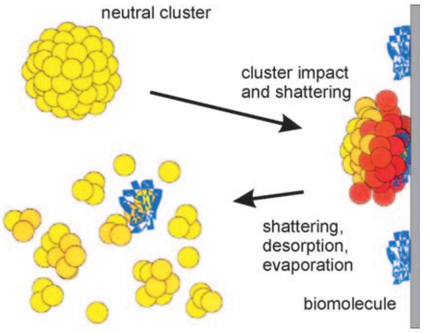
The big "DIP"per: The preparation of both L,L-DIP and L,D-DIP (see structures) involves a complex case of double asymmetric induction in the key step of the synthesis. The differential ability of each isomer to contribute to thermoprotection in the context of a key enzyme has been assessed and both isomers of DIP are shown to possess biological activity.

Mass Spectrometry

C. R. Gebhardt,* A. Tomsic, H. Schröder, M. Dürr,* K. L. Kompa ______ **4162 – 4165**

Matrix-Free Formation of Gas-Phase Biomolecular Ions by Soft Cluster-Induced Desorption

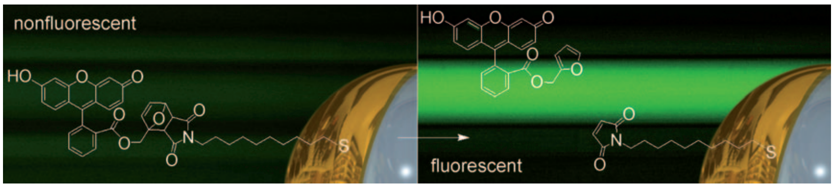
All in a ball: Neutral molecular clusters consisting of a few thousand molecules can be seen as tiny snow balls; if they are thrown fast enough onto a surface, they are able to pick up biomolecules such as insulin from that surface. Since they break down and evaporate during and after the collision, bare biomolecular ions are available for mass spectrometry after such an energetic throw.



Photothermal Release

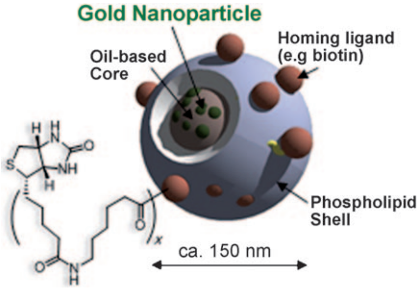
A. B. S. Bakhtiari, D. Hsiao, G. Jin, B. D. Gates,* N. R. Branda* **4166 – 4169**

An Efficient Method Based on the Photothermal Effect for the Release of Molecules from Metal Nanoparticle Surfaces



Please release me: The heat generated when metal nanoparticles absorb light results in a significant increase in the temperature of the environment around the particles and is used to selectively break bonds within a molecular system anchored to the nanoparticle surface (see picture). This process represents an advantageous and more universal method to deliver chemicals locally, while avoiding excessive tissue damage.

Spotting clots: Vascularly constrained colloidal gold nanobeacons (GNBs; see picture) can be used as exogenous photoacoustic contrast agents for the targeted detection of fibrin, a major biochemical feature of thrombus. Fibrin-targeted GNBs provide a more than tenfold signal enhancement in photoacoustic tomography in the near-IR wavelength window, indicating their potential for diagnostic imaging.



Functional Nanobeacons

D. Pan,* M. Pramanik, A. Senpan, X. Yang, K. H. Song, M. J. Scott, H. Zhang, P. J. Gaffney, S. A. Wickline, L. H. V. Wang,* G. M. Lanza **4170 – 4173**

Molecular Photoacoustic Tomography with Colloidal Nanobeacons

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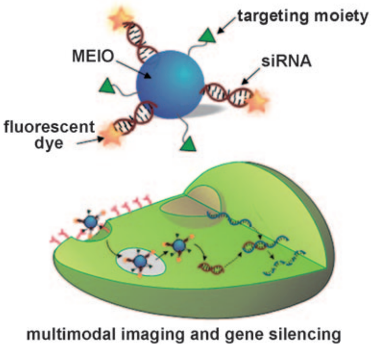


Cancer-cell-targeted gene silencing was observed with a magnetic-nanoparticle platform (MEIO, magnetism-engineered iron oxide) on which a fluorescent dye, siRNA, and a RGD-peptide targeting moiety were attached (see picture). The different functionalities enable the macroscopic (magnetic resonance) and microscopic (fluorescence) imaging of target cells. This system may be suitable for concurrent diagnostic and therapeutic applications.

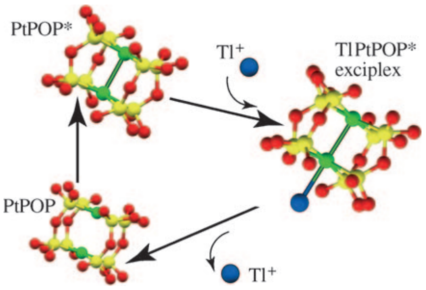
Bionanotechnology

J.-H. Lee, K. Lee, S. H. Moon, Y. Lee, T. G. Park,* J. Cheon* **4174 – 4179**

All-in-One Target-Cell-Specific Magnetic Nanoparticles for Simultaneous Molecular Imaging and siRNA Delivery

---

Molecular movies: Time-resolved X-ray scattering provides direct structural information on an electronically excited complex while it is formed in the bimolecular reaction between excited octahydrogen[tetrakis-μ-diphosphito-1κP:2κP′-diplatinate](4-) (PtPOP*) and thallium ions. In the exciplex one thallium(I) and two platinum(II) ions are found to be collinear.



Excited-State Structures

K. Haldrup, M. Christensen, M. Cammarata, Q. Kong, M. Wulff, S. O. Mariager, K. Bechgaard, R. Feidenhans'l, N. Harrit,* M. M. Nielsen* **4180 – 4184**

Structural Tracking of a Bimolecular Reaction in Solution by Time-Resolved X-Ray Scattering

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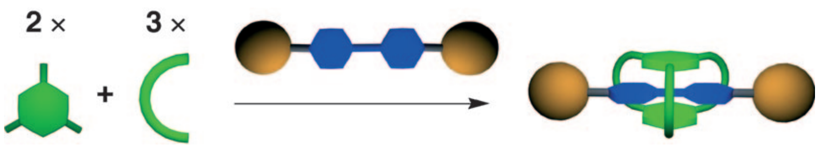


Cage me! A linear dumbbell-shaped bipyridinium molecule can template cage formation around itself through sixfold imine bond formation to give an interlocked [2]rotaxane as the single product (see picture). This highly efficient [2+3] clipping occurs despite the symmetry mismatch between the template and the formed macrobicycle.

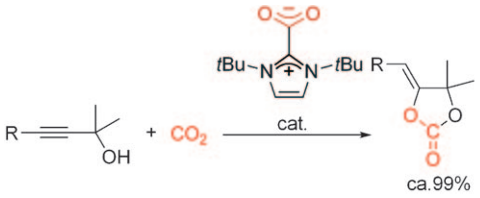
Supramolecular Chemistry

L. M. Klivansky, G. Koshkakaryan, D. Cao, Y. Liu* **4185 – 4189**

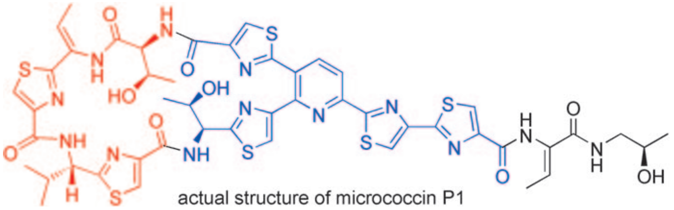
Linear π-Acceptor-Templated Dynamic Clipping to Macrobicycles and [2]Rotaxanes

The time is ripe: A general theoretical framework based on force-transformed potential energy surfaces rationalizes the intriguing results of recent experiments in the emerging field of covalent mechanochemistry.

> Ist es der Sinn, der alles wirkt und schafft?
> Es sollte stehn: Im Anfang war die Kraft!
>
> *Faust – Der Tragödie erster Teil*
> *Johann Wolfgang von Goethe*

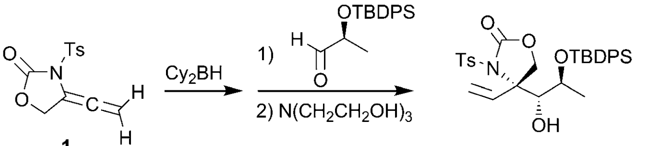


Getting a fix: N-heterocyclic carbenes (NHCs) and NHC–CO_2 adducts serve as potent organocatalysts for carbonate synthesis by the addition of a CO_2 unit to propargylic alcohols or epoxides under mild and solvent-free reaction conditions (see scheme). The enhanced Lewis basicity of imidazol-2-ylidenes bearing electron-donating alkyl groups on the nitrogen atoms leads to utilizing CO_2 as a nucleophilic fragment in the chemical fixation processes.



actual structure of micrococcin P1

Fifty years after the discovery of the thiopeptide antibiotic micrococcin P1, the constitutional and stereochemical uncertainties concerning its structure have been lifted with its total synthesis and absolute stereochemical assignment (see picture).



1

95% yield, >95% *ee*

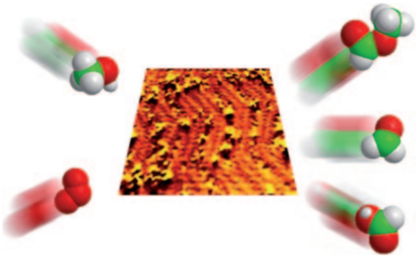
Three in a row! Highly functionalized quaternary amino polyols with three consecutive asymmetric carbon centers have been prepared through tandem hydroboration of allene **1** and addition to an aldehyde (see scheme; Cy = cyclohexyl, TBDPS = *tert*-butyldiphenylsilyl, Ts = 4-toluenesulfonyl). This one-pot process provides access to advanced intermediates for the enantioselective synthesis of α-substituted serines.

Alcohol Oxidation

VIP

B. Xu, X. Liu, J. Haubrich, R. J. Madix, C. M. Friend* —— **4206–4209**

Selectivity Control in Gold-Mediated Esterification of Methanol

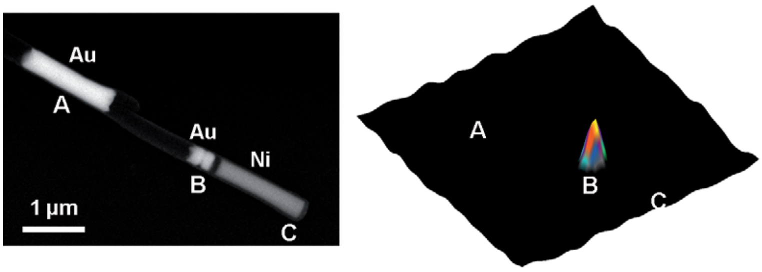


The Midas touch: The low-temperature transformation of methanol to methyl formate, formaldehyde, and formic acid is promoted by atomic oxygen adsorbed on metallic gold (see picture). The reactions occur with O-containing Au nanoparticles formed on Au(111) upon oxidation with ozone at 200 K; the facile esterification to methyl formate occurs well below room temperature.

Surface Analysis

W. Wei, S. Li, J. E. Millstone, M. J. Banholzer, X. Chen, X. Xu, G. C. Schatz,* C. A. Mirkin* **4210–4212**

Surprisingly Long-Range Surface-Enhanced Raman Scattering (SERS) on Au–Ni Multisegmented Nanowires

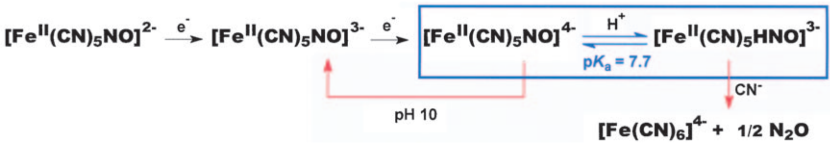


Very long range surface-enhanced Raman scattering is observed from a nickel nanowire that is separated by 120 nm from a pair of gold nanodisks. The excitation of the surface-plasmon resonance (SPR) from the gold nanodisk pair generates an enhanced electromagnetic field near the nickel segment (SEM, left), leading to Raman intensity greater than the nickel alone (right).

Nitroxyl Complexes

A. C. Montenegro, V. T. Amorebieta, L. D. Slep, D. F. Martín, F. Roncaroli, D. H. Murgida, S. E. Bari,* J. A. Olabe* —— **4213–4216**

Three Redox States of Nitrosyl: NO⁺, NO•, and NO⁻/HNO Interconvert Reversibly on the Same Pentacyanoferrate(II) Platform



Not so elusive: $[Fe^{II}(CN)_5(HNO)]^{3-}$ has been characterized spectroscopically after the two-electron reduction of nitroprusside (see scheme). The complex is stable at pH 6, slowly decomposing to $[Fe(CN)_6]^{4-}$ and N_2O. It is deprotonated at increasing pH value with oxidation of bound NO^- to $[Fe^{II}(CN)_5(NO)]^{3-}$. $[Fe^{II}(CN)_5(HNO)]^{3-}$ is the first non-heme iron–nitroxyl complex prepared in aqueous solution that is reversibly redox-active under biologically relevant conditions.

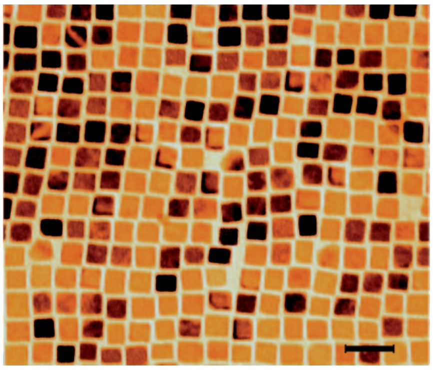
Electrocatalysis

VIP

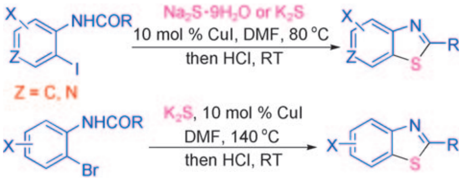
D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang,* S. Zou,* K. Sun — **4217–4221**

Solution-Based Evolution and Enhanced Methanol Oxidation Activity of Monodisperse Platinum–Copper Nanocubes

Shape-controlled catalysis: High-quality Pt–Cu nanocubes with an average size of about 8 nm (see picture, scale bar = 20 nm) were synthesized from a high-temperature organic solution system in the presence of various capping ligands. These cubic Pt–Cu nanocrystals terminated with {100} facets demonstrated a superior catalytic activity towards methanol oxidation compared to similar sized Pt–Cu and Pt nanospheres.

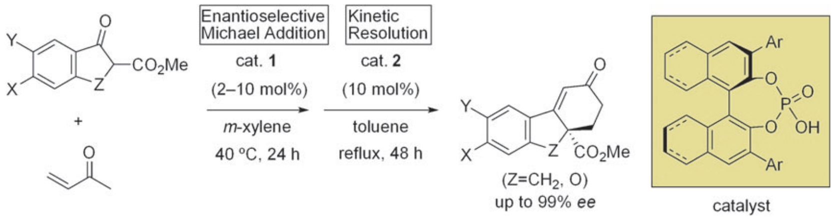


Heterocycles



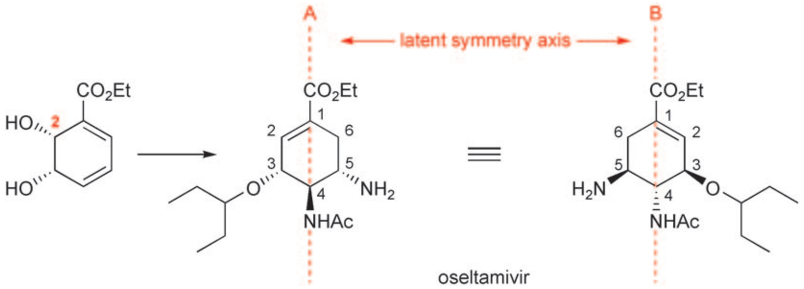
Don't tell azole: The first metal-catalyzed direct coupling of metal sulfides with aryl halides and subsequent intramolecular condensation provided substituted benzothiazoles (see scheme). A wide range of functional groups are tolerated under the reaction conditions.

Organocatalysis



Let's resolve our differences: Implementation of an enantioselective Michael addition followed by an intramolecular aldol reaction catalyzed by two phosphoric acids has enabled the synthesis of cyclohexenone derivatives with excellent enantioselectivities. Prominent kinetic resolution was observed in the latter reaction. Ar = aromatic group, X = H, halogen, Y = H, Me, halogen.

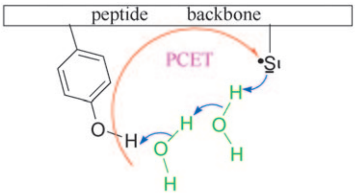
Tamiflu Synthesis



A short chemoenzymatic formal synthesis of oseltamivir from ethyl benzoate has been achieved. The key steps involve a toluene dioxygenase-mediated dihydroxylation, hetero-Diels–Alder cycloaddition, and generation of C4 acetamido functionality. The formal synthesis of oseltamivir is achieved in ten steps and incorporates a unique translocation of the olefin with concomitant elimination of the C2 hydroxy group (see scheme).

Electron Transfer

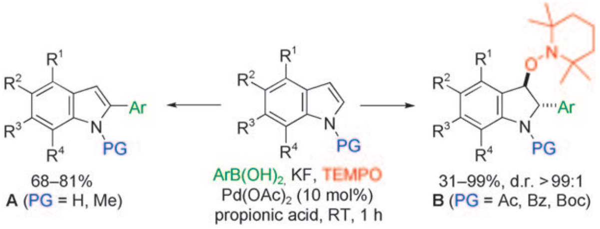
Caught on the hop: In multistep electron transfer (ET) reactions through peptides, aliphatic amino acids can also act as relay stations. With cysteine, the reaction occurs as a proton-coupled electron transfer (PCET) with water used as a mediator for the proton transfer (see picture).



Synthetic Methods

S. Kirchberg, R. Fröhlich,
A. Studer* ________ **4235–4238**

Stereoselective Palladium-Catalyzed Carboaminoxylations of Indoles with Arylboronic Acids and TEMPO

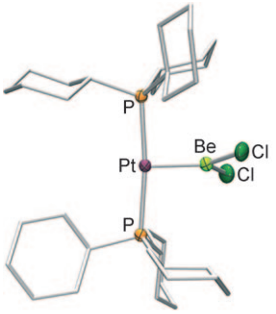


Indoles are not indolent: Various indoles react with arylboronic acids chemodivergently. C–H arylation of free indole and *N*-methylindole gives the corresponding C(2)-arylated indoles **A** whereas N-acylated, N-benzoylated, and N-Boc-protected indoles provide the corresponding arylcarboaminoxylated products **B** with excellent diastereoselectivity in good to excellent yields.

Beryllium Ligands

H. Braunschweig,* K. Gruss,
K. Radacki ________ **4239–4241**

Complexes with Dative Bonds between d- and s-Block Metals: Synthesis and Structure of $[(\mathrm{Cy_3P})_2\mathrm{Pt{-}Be(Cl)X}]$ ($\mathrm{X = Cl, Me}$)

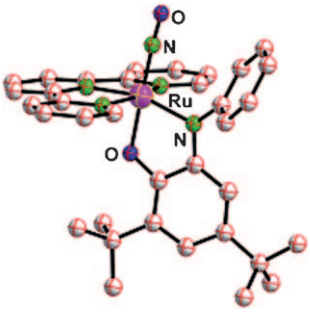


A platinum–beryllium adduct (see structure) was prepared by the reaction of $[\mathrm{Pt(PCy_3)_2}]$ and $\mathrm{BeCl_2}$. Treatment with methyllithium resulted in ligand substitution at the beryllium center. Both complexes were structurally characterized and display unprecedented two-center two-electron bonds between a transition metal and beryllium.

Redoxactive Ligands

A. K. Das, B. Sarkar, C. Duboc, S. Strobel,
J. Fiedler, S. Záliš, G. K. Lahiri,
W. Kaim* ________ **4242–4245**

An Odd-Electron Complex $[\mathrm{Ru}^k(\mathrm{NO}^m)(\mathrm{Q}^n)(\mathrm{terpy})]^{2+}$ with Two Prototypical Non-Innocent Ligands

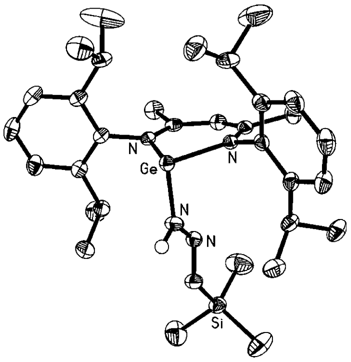


Six combinations of oxidation states are conceivable for the paramagnetic title complex. Single-crystal X-ray diffraction, spectroscopic analysis (IR, EPR at conventional and high frequency), and DFT calculations establish that it is the iminosemiquinone radical structure that is formed: $[\mathrm{Ru}^k(\mathrm{NO}^m)(\mathrm{Q}^n)(\mathrm{terpy})]^{2+}$ ($k = 2+$, $m = 1+$, $n = 1-$).

Nitrogen Insertion

A. Jana, S. S. Sen, H. W. Roesky,*
C. Schulzke, S. Dutta,
S. K. Pati ________ **4246–4248**

End-On Nitrogen Insertion of a Diazo Compound into a Germanium(II) Hydrogen Bond and a Comparable Reaction with Diethyl Azodicarboxylate



A happy ending: The germanium(II) hydride [LGeH], where $\mathrm{L} = [\mathrm{HC}\{(\mathrm{CMe})(2,6\text{-}i\mathrm{Pr_2C_6H_3N})\}_2]$, reacts with a diazoalkane to form the hydrazone derivative (see picture). The reaction proceeds through the unprecedented end-on nitrogen insertion of the diazo compound.

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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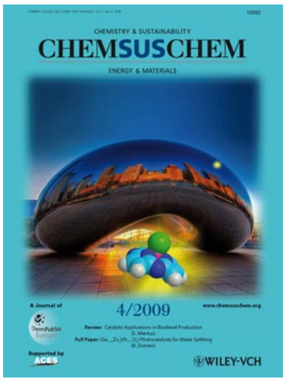

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