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. Staubitz, A. Presa, I. Manners**
Iridium-Catalyzed Dehydrocoupling of Primary Amine–Borane Adducts: A Route to High Molecular Weight Polyaminoboranes, Boron–Nitrogen Analogues of Polyolefins

S. Gerlich, M. Gring, H. Ulbricht, K. Hornberger, J. Tüxen, M. Mayor,* M. Arndt**
Matter-Wave Metrology as a Complementary Tool for Mass Spectrometry

*T. Gupta, M. E. van der Boom**
Redox-Active Monolayers as a Versatile Platform for Integrating Boolean Logic Gates

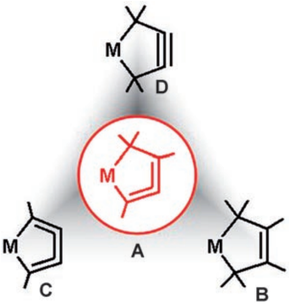
V. L. Blair, L. M. Carrella, W. Clegg, B. Conway, R. W. Harrington, L. M. Hogg, J. Klett, R. E. Mulvey, E. Rentschler, L. Russo*
Tuning the Basicity of Synergic Bimetallic Reagents: Switching the Regioselectivity of Direct Dimetalation of Toluene from 2,5- to 3,5- Positions

News

Books

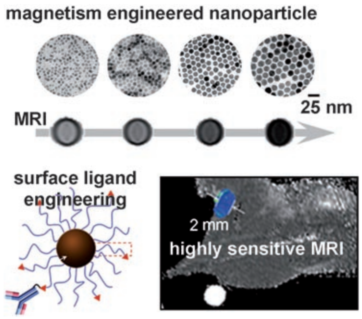
Highlights

In the loop: Highly strained five-membered metallacycles, until very recently uncharted territory, are currently receiving much attention in organometallic chemistry. Recent publications are discussed in which the theoretically predicted 1-metallacyclopenta-2,3-dienes **A** are attained, filling the gap between 1-metallacyclopent-3-enes **B** and 1-metallacyclopenta-2,3,4-trienes **C**.



Unusual Metallacycles

Reviews



Tailor made: Owing to their unique magnetic properties and being a size comparable to biological functional units, tailored magnetic nanoparticles (MNPs) are increasingly used as medical probes. Their use enables the sensitive and target specific observation of biological events at the molecular and cellular levels.

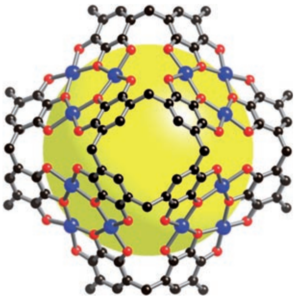
Magnetic Nanoparticles

Contents

Metal–Organic Polyhedra

D. J. Tranchemontagne, Z. Ni,
M. O'Keeffe,* O. M. Yaghi* **5136–5147**

Reticular Chemistry of Metal–Organic Polyhedra



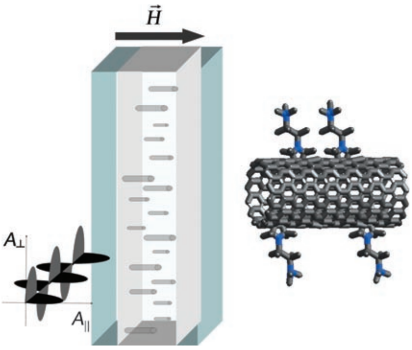
Made to measure: Analysis of structures of existing metal–organic polyhedra (MOPs) delivers important criteria for the design of new MOPs. The angle between the links from the secondary building unit and that between the links of a ditopic linker linker are important parameters for the design of such structures.

Communications

Nanotechnology

J. Tumpane,* N. Karousis,
N. Tagmatarchis, B. Nordén **5148–5152**

Alignment of Carbon Nanotubes in Weak Magnetic Fields

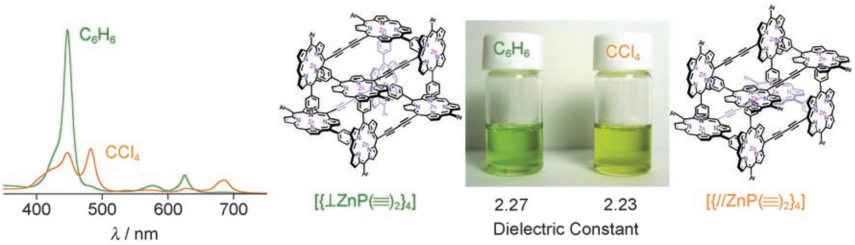


Gently brought into line: Functionalized carbon nanotubes (see picture, C,H black, N blue) facilitate a high degree of orientation in a weak magnetic field $\vec{H}$, as detected by linear dichroism spectroscopy (incident planes of light $A_\perp$ and $A_\parallel$). In addition, relaxation measurements in the magnetic field allow the length of the nanotubes to be determined.

Molecular Recognition

J. Aimi, Y. Nagamine, A. Tsuda,*
A. Muranaka, M. Uchiyama,
T. Aida* ______________ **5153–5156**

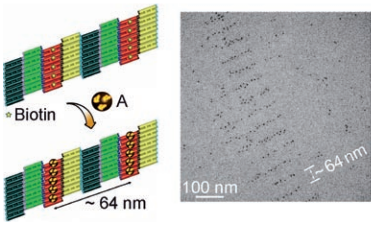
"Conformational" Solvatochromism: Spatial Discrimination of Nonpolar Solvents by Using a Supramolecular Box of a π-Conjugated Zinc Bisporphyrin Rotamer



Boxing clever: A cyclic tetramer of the dialkynylene-bridged zinc bisporphyrin rotamer $[\mathrm{ZnP}(\equiv)_2]$ shows a unique solvatochromic response to nonpolar solvents with equally low dielectric constants (2.23–2.57). This solvatochromism originates from the π conjugation of $[\mathrm{ZnP}(\equiv)_2]$. The tetramer $[\{\mathrm{ZnP}(\equiv)_2\}_4]$ can discriminate spectroscopically benzene from CCl_4 (see picture) and even the regioisomers of xylene.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/ sales tax.

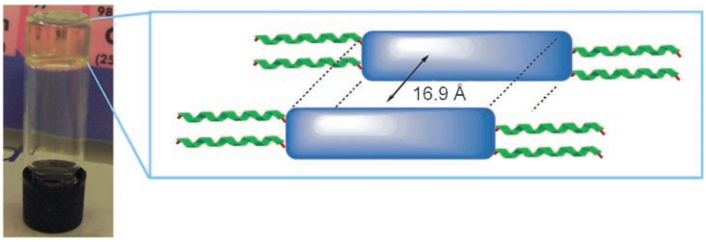
Turning dots into stripes: Rationally designed DNA-tile arrays are used to organize quantum dots into well-aligned two-dimensional nanopatterns (see schematic representation and TEM image; A: streptavidin-coated quantum dots); the power of programmable DNA scaffolding is thereby demonstrated.



Quantum Dots

J. Sharma, Y. Ke, C. Lin, R. Chhabra, Q. Wang, J. Nangreave, Y. Liu,* H. Yan* **5157 – 5159**

DNA-Tile-Directed Self-Assembly of Quantum Dots into Two-Dimensional Nanopatterns

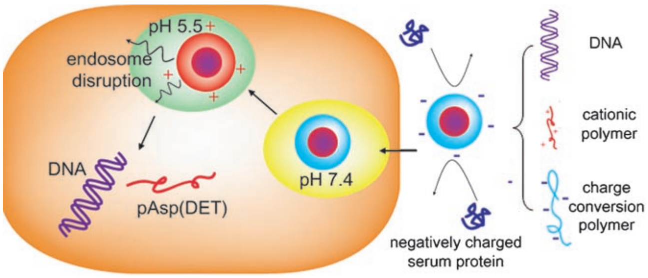


Peptide Organogels

M. I. Gibson, N. R. Cameron* **5160 – 5162**

Organogelation of Sheet–Helix Diblock Copolypeptides

Together they're strong: Block copolypeptides containing poly(benzyl-L-threonine) and an α-helical block are effective organogelators despite the high solubility of the constituent homopolymers. An unexpected conformational change in the first block, from random coil to β sheet, directs the assembly into stacked lamellae (see picture).



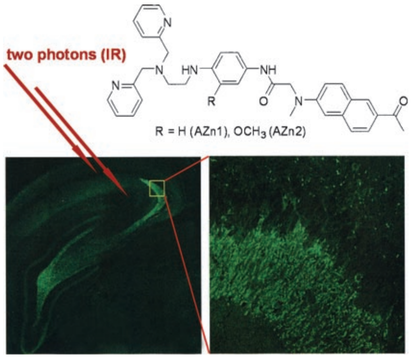
Cell Transfection

Y. Lee, K. Miyata, M. Oba, T. Ishii, S. Fukushima, M. Han, H. Koyama, N. Nishiyama, K. Kataoka* **5163 – 5166**

Charge-Conversion Ternary Polyplex with Endosome Disruption Moiety: A Technique for Efficient and Safe Gene Delivery

Wrapped for special delivery: A ternary polyplex, with an endosomal disruption moiety based on the charge-conversion polymer pAsp(DET-Aco), showed negative charges for serum stability and low cytotoxicity, but the charges became positive and the endosome disruption moiety was exposed (see picture). High transfection efficiency and minimal cytotoxicity were observed with primary cells.

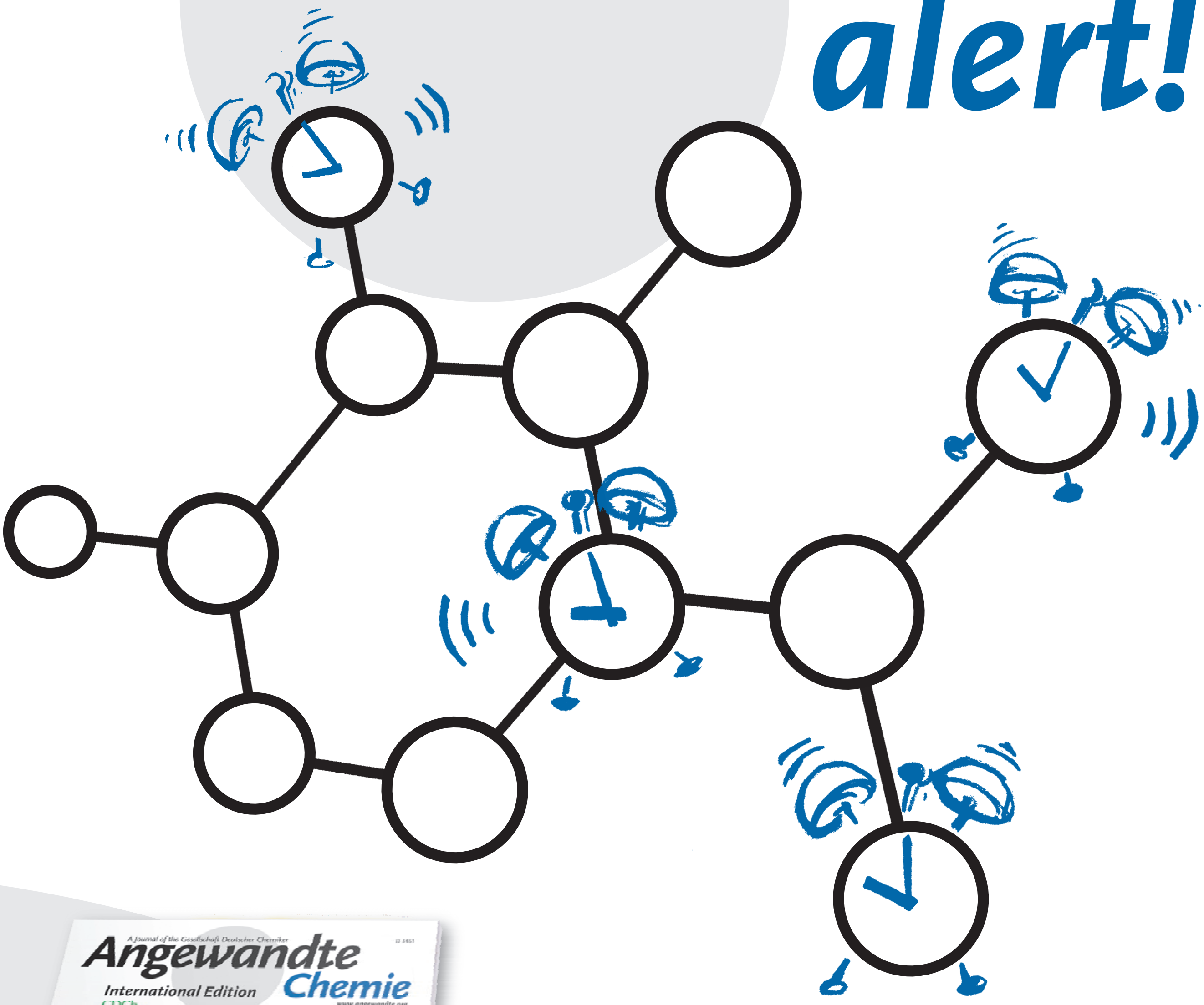
The living image: The efficient two-photon probes AZn1 and AZn2 (see picture for rat brain tissue) show 24- to 52-fold two-photon excited fluorescence enhancement in response to Zn^{2+}. They can selectively detect intracellular free Zn^{2+} ions in live cells and in living tissues at a depth of 80–150 μm without interference from other metal ions and the membrane-bound probes.



Fluorescent Probes

H. M. Kim, M. S. Seo, M. J. An, J. H. Hong, Y. S. Tian, J. H. Choi, O. Kwon, K. J. Lee, B. R. Cho* **5167 – 5170**

Two-Photon Fluorescent Probes for Intracellular Free Zinc Ions in Living Tissue

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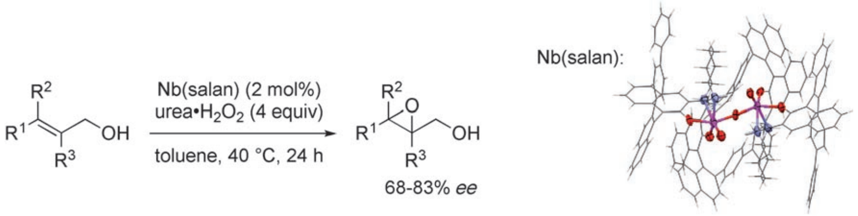
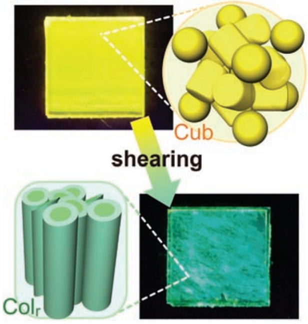
2008–47/6
Diamondoid Chemistry
A. A. Fokin, P. R. Schreiner, and H. Schwertfeger
Hugo Schiff
T. T. Tidwell
Highlights: Light Harvesters · Structure of Water
ACIEFS 47 (6) 987–1152 (2008) · ISSN 1433-7851 · Vol. 47 · No. 6
WILEY-VCH

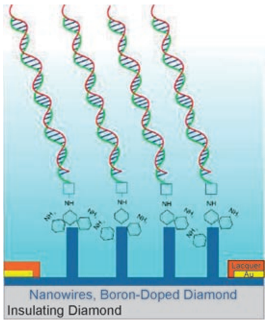


Bridging the catalyst: The dimeric complex [(μ-oxo){Nb(salan)}$_2$] catalyzes asymmetric epoxidation of allylic alcohols by hydrogen peroxide to give epoxy alcohols with good to high enantioselectivities irrespective of the olefin geometry (see scheme).



Shear brilliance: The photoluminescent color of a pyrene-based liquid crystal changes from yellow to blue-green upon mechanical shearing due to a phase transition from a micellar cubic to a columnar phase (see picture).

Le Tour de MTO: A complete working catalytic cycle for the conversion of methanol to olefins in HZSM-5 is reported in full consistency with both experimental and theoretical observations. This particular route includes carbon-atom scrambling into a methylbenzene ring, NMR-observed cationic intermediates, and the production of isobutene.



Live wire: Biofunctionalized vertically aligned diamond nanowires as DNA sensors benefit from the outstanding electrochemical properties of diamond as a transducer as well as the advantages of dispersed, controlled binding of linker molecules to achieve behavior of DNA molecules' "like-in-solution" situation.

Biosynthesis of Nanoparticles

S. H. Kang, K. N. Bozhilov, N. V. Myung, A. Mulchandani, W. Chen* **5186–5189**

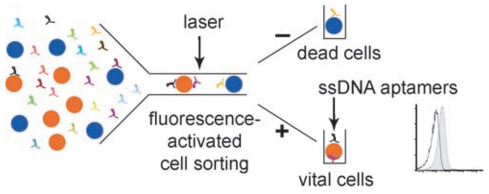
Microbial Synthesis of CdS Nanocrystals in Genetically Engineered *E. coli*

A bacterial biofactory: *Escherichia coli* strains were genetically engineered to produce phytochelatins (PCs) as capping agents and used for the intracellular synthesis of fluorescent and water-soluble PC-coated CdS nanoparticles (see figure). The size of the semiconductor nanocrystals could be tuned by controlling the population of the capping PCs. SpPCS is the PC synthase from *Schizosaccharomyces pombe*; GSHI* = γ-glutamylcysteine synthetase.

Cell Recognition

M.-S. L. Raddatz, A. Dolf, E. Endl, P. Knolle, M. Famulok,* G. Mayer* **5190–5193**

Enrichment of Cell-Targeting and Population-Specific Aptamers by Fluorescence-Activated Cell Sorting



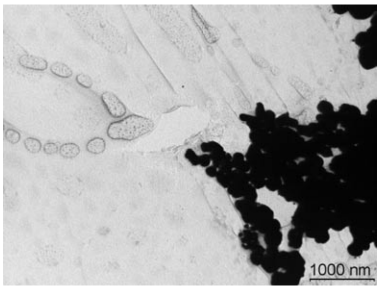
A class above: In a sophisticated approach to the systematic evolution of ligands by exponential enrichment (SELEX) of cell-type-specific nucleic acid aptamers, the title technique was combined with the use of combinatorial nucleic acid libraries to target a defined subpopulation within composite mixtures of cells (see picture). The ssDNA library after 10 selection cycles bound vital Burkitt lymphoma cells more effectively than the starting library.

Gold Catalyst for Diboration

J. Ramírez, M. Sanaú, E. Fernández* **5194–5197**

Gold(0) Nanoparticles for Selective Catalytic Diboration

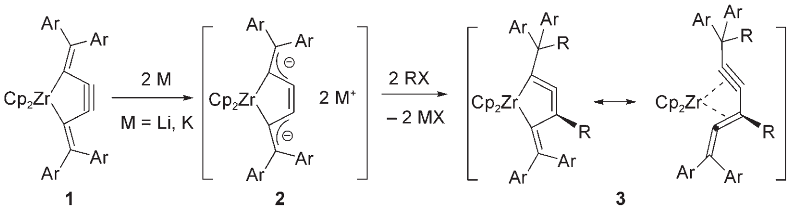
Going with gold: Gold(0) nanoparticles stabilized with the diphosphine ligand binap mediate the catalytic diboration of styrene, resulting in complete formation of the bis(boronate)ester product. The gold(0) catalytic mechanism can involve base-assisted heterolytic cleavage of diboron reagents followed by the transmetalation step.



Metallacyclopentynes

N. Suzuki,* D. Hashizume, H. Koshino, T. Chihara **5198–5202**

Transformation of a 1-Zirconacyclopent-3-yne, a Five-Membered Cycloalkyne, into a 1-Zirconacyclopent-3-ene and Formal “1-Zirconacyclopenta-2,3-dienes”



Alkyne, alkene, and “allene”? A stable five-membered metallacycloalkyne **1** with alkylidene moieties was treated with an alkali metal to give a dianionic species **2**, which was transformed into a 1-zirconacyclopent-3-ene complex by protonation. The alkylation of **2** afforded zirconocene–η^4-1,3-enyne complexes **3**, which can be regarded as formal “1-zirconacyclopenta-2,3-dienes”. Ar = 4-EtC$_6$H$_4$; R = Me, Me$_3$Sn.

Skeletal Rearrangement

K. Ohmatsu, T. Tanaka, T. Ooi,
K. Maruoka* ——— 5203 – 5206

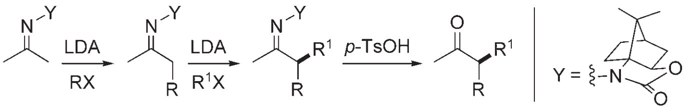
Complete Switch of Migratory Aptitude in Aluminum-Catalyzed 1,2-Rearrangement of Differently α,α-Disubstituted α-Siloxy Aldehydes

Control of the migration tendency: The regiodivergent 1,2-rearrangement of α-siloxy aldehydes bearing α-aryl and α-alkyl substituents into α-siloxy ketones has been realized by using different aluminum Lewis acid catalyst/solvent systems (see scheme). The scope of this unprecedented protocol has been investigated with various substrates and clearly demonstrates its utility for the selective synthesis of two structural isomers from one substrate.

Asymmetric Synthesis

D. Lim, D. M. Coltart* ——— 5207 – 5210

Simple and Efficient Asymmetric α-Alkylation and α,α-Bisalkylation of Acyclic Ketones by Using Chiral N-Amino Cyclic Carbamate Hydrazones

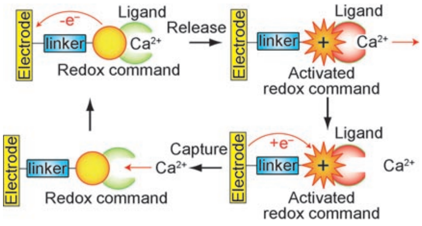


Distinguishing left from right: In the title reactions, chiral N-amino cyclic carbamates (ACCs) substantially diminish the drawbacks associated with the use of chiral dialkyl hydrazines, yet provide excellent stereoselectivity and high yields. In addition, ACCs exhibit a unique directing effect that overrides the inherent selectivity of lithium diisopropylamide (LDA) and enables the asymmetric α,α-bisalkylation of ketones (see scheme).

Electrochemistry

C. Amatore,* D. Genovese,
E. Maisonhaute,* N. Raouafi,
B. Schöllhorn* ——— 5211 – 5214

Electrochemically Driven Release of Picomole Amounts of Calcium Ions with Temporal and Spatial Resolution

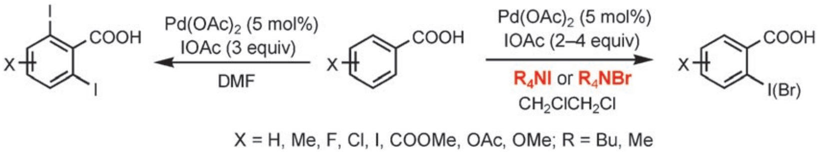


Controlled delivery: Redox commutation of a paraphenylenediamine and aza-crown ether assembly anchored as a self-assembled monolayer to an electrode surface allows the time and spatially controlled release of picomole amounts of calcium ions. The release occurs on a sub-millisecond time scale, and is irreversible provided that the two-electron-oxidized redox center is not returned electrochemically to its neutral initial state (see scheme).

C–H Activation

T.-S. Mei, R. Giri, N. Maugel,
J.-Q. Yu* ——— 5215 – 5219

$\mathrm{Pd^{II}}$-Catalyzed Monoselective *ortho* Halogenation of C–H Bonds Assisted by Counter Cations: A Complementary Method to Directed *ortho* Lithiation

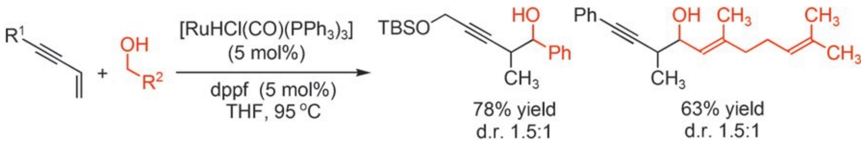


When the counterion counts: The yield and selectivity of the title transformation of benzoic acid derivatives were improved greatly by using tetraalkyl ammonium salts as additives (see scheme; monoselectivity: 5:1–18:1). These effects are attributed to the influence of counter cations. The halogenated products are versatile intermediates for the construction of substituted aromatic compounds. DMF = *N*,*N*-dimethylformamide.

Ruthenium Catalysis

R. L. Patman, V. M. Williams, J. F. Bower, M. J. Krische* ________ 5220 – 5223

Carbonyl Propargylation from the Alcohol or Aldehyde Oxidation Level Employing 1,3-Enynes as Surrogates to Preformed Allenylmetal Reagents: A Ruthenium-Catalyzed C–C Bond-Forming Transfer Hydrogenation

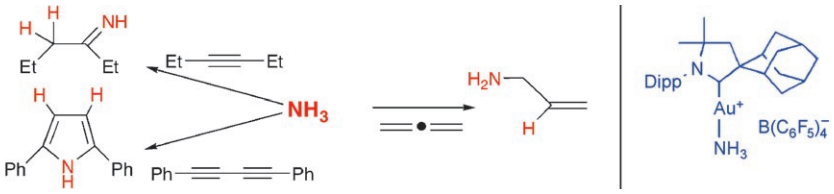


Transcending oxidation level: Under the conditions of ruthenium-catalyzed transfer hydrogenation, conjugated enynes couple to benzylic, allylic, and aliphatic alcohols or aldehydes to furnish products of carbonyl propargylation (see scheme; dppf = 1,1′-bis(diphenylphosphino)ferrocene, TBS = *tert*-butyldimethylsilyl). Isotopic labeling studies corroborate a mechanism involving hydrogen donation from the alcohol to the enyne.

C–N Bond Formation

V. Lavallo, G. D. Frey, B. Donnadieu, M. Soleilhavoup, G. Bertrand* ________ 5224 – 5228

Homogeneous Catalytic Hydroamination of Alkynes and Allenes with Ammonia

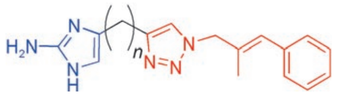


A golden ticket to the synthesis of reactive nitrogen-containing compounds, such as imines, enamines, and allyl amines, through the addition of NH_3 to unsaturated bonds is the cationic cyclic (alkyl)(amino)carbene–gold(I) catalyst shown in blue (Dipp = diisopropylphenyl). An ideal initial step for the preparation of simple bulk chemicals, this reaction is also useful for the synthesis of more complex molecules (see examples).

Click Chemistry

S. A. Rogers, C. Melander* 5229 – 5231

Construction and Screening of a 2-Aminoimidazole Library Identifies a Small Molecule Capable of Inhibiting and Dispersing Bacterial Biofilms across Order, Class, and Phylum

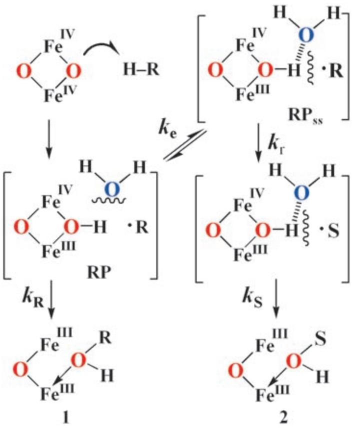


A team of three: 2-Aminoimidazole, triazole, and tether units together resulted in conjugates (see picture, $n = 4–6$ for the most active compounds) that are capable of inhibiting and dispersing bacteria biofilms without inducing bacterial death. Such biofilms have been implicated in a plethora of medical problems, including infection of implanted medical devices and the mortality of cystic fibrosis patients.

Enzyme Mechanisms

R. N. Austin,* K. Luddy, K. Erickson, M. Pender-Cudlip, E. Bertrand, D. Deng, R. S. Buzdygon, J. B. van Beilen, J. T. Groves* ________ 5232 – 5234

Cage Escape Competes with Geminate Recombination during Alkane Hydroxylation by the Diiron Oxygenase AlkB

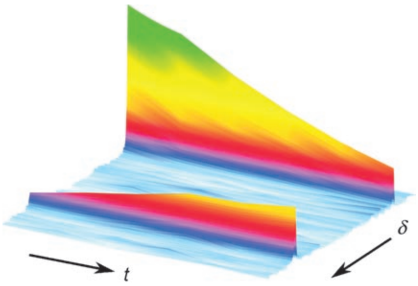


AlkB stops the radical clock: Three structurally analogous radical-clock substrates with a large span in their rearrangement rates are hydroxylated by AlkB to afford similar amounts of rearranged (**2**) and unrearranged products (**1**). Such a result is in accord with radical rebound competing with cage escape of the geminate substrate radical. The results show that radical clocks can measure both the radical lifetime and the kinetics of cage escape.

NMR Spectroscopy

S. Bowen, C. Hilty* ______ 5235 – 5237

Time-Resolved Dynamic Nuclear Polarization Enhanced NMR Spectroscopy



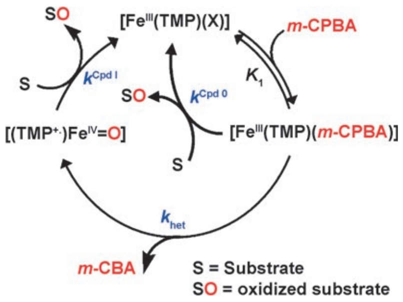
The sensitive touch: Sensitivity constraints in NMR spectroscopy typically call for long measurement times. Hyperpolarization can enhance the time resolution of NMR spectroscopy by removing the need for signal averaging. Reactions such as enzyme catalysis can be followed in real time by hyperpolarized NMR spectroscopy through reduction in the intensity of the substrate resonance as well as the appearance of product resonances (see picture).

Bioinorganic Chemistry

A. Franke, C. Fertinger,
R. van Eldik* ______ 5238 – 5242

Which Oxidant Is Really Responsible for P450 Model Oxygenation Reactions? A Kinetic Approach

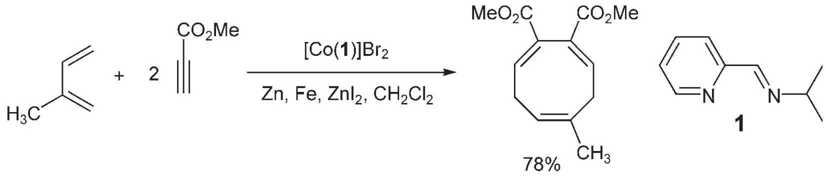
A rate-fate fête: Direct kinetic studies on epoxidation and sulfoxidation reactions revealed that the oxygenating capability of [(TMP$^{+\bullet}$)Fe^{IV}=O] is orders of magnitude higher than that of [Fe^{III}(TMP)(*m*-CPBA)]. Under catalytic turnover conditions, the relative ratio between the rate of O–O bond heterolytic cleavage and the rate of oxygen transfer from the [Fe^{III}(TMP)(*m*-CPBA)] intermediate to the substrate, should be taken into consideration. *m*-CPBA = *m*-chloroperbenzoic acid, TMP = *meso*-tetramesitylporphyrin.



Cycloaddition Reactions

G. Hilt,* J. Janikowski ______ 5243 – 5245

Cobalt-Catalyzed [4+2+2] Cycloaddition for the Synthesis of 1,3,6-Cyclooctatrienes

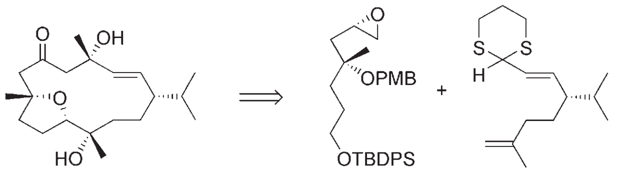


After eight? Polysubstituted 1,3,6-cyclooctatrienes can be obtained in high regioselectivity and in good yields from a cobalt-catalyzed intermolecular cycloaddition reaction between two alkynes and a 1,3-diene (see example in scheme).

Natural Product Synthesis

L. F. Tietze,* C. C. Brazel, S. Hölsken,
J. Magull, A. Ringe ______ 5246 – 5249

Total Synthesis of Polyoxygenated Cembrenes



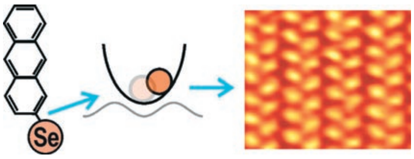
A convergent approach for the stereoselective construction of polyoxygenated cembrenes is reported. Key steps in the synthesis are an asymmetric domino multicomponent allylation, a modified Myers α-alkylation, and a ring-closing metathesis.

Surface Chemistry

A. Bashir, D. Käfer, J. Müller, C. Wöll,
A. Terfort, G. Witte* ———— 5250–5252

Selenium as a Key Element for Highly Ordered Aromatic Self-Assembled Monolayers

Less stress: Self-assembled monolayers of aromatic molecules become significantly better ordered, if selenium atoms instead of sulfur atoms are used as anchoring groups. Presumably as a result of a lowered corrugation for the Au–Se interaction, the molecules can adapt more easily to structures governed by the carbon backbone.

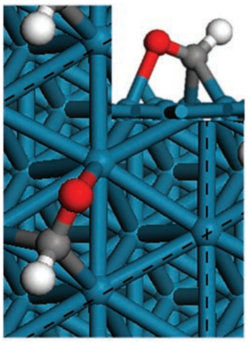


Biofuels

O. R. Inderwildi,* S. J. Jenkins,
D. A. King ———— 5253–5255

Mechanistic Studies of Hydrocarbon Combustion and Synthesis on Noble Metals

Common staging point: Results of DFT studies on surface-catalyzed processes indicate that oxymethylidyne species (CHO) are intermediates in both the combustion and the synthesis of hydrocarbons on noble-metal surfaces (the picture shows CHO formation on Pd). Combustion and synthesis proceed by very similar pathways, but in opposite directions, even though different metals are used in the two processes.



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

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