## *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:*

*Y. H. Sehlleier, A. Verhoeven, M. Jansen**
**Observation of Direct Bonds Between Carbon and Nitrogen in Si–B–N–C Ceramic After Pyrolysis at 1400 °C**

*H. Braunschweig,* C. J. Adams, T. Kupfer, I. Manners, R. Richardson, G. R. Whittell*
**A Paramagnetic Polymer by Ring-Opening Polymerization of a Strained [1]Vanadoarenophane**

*W. D. Pyrz, D. A. Blom, T. Vogt, D. J. Buttrey**
**Direct Imaging of the MoVTeNbO M1 Phase Using an Aberration-Corrected High-Resolution Scanning Transmission Electron Microscope**

*Q. Zhang, T. P. Chou, B. Russo, S. A. Jenekhe, G. Cao**
**Aggregation of ZnO Nanocrystallites for High Conversion Efficiency in Dye-Sensitized Solar Cells**

*S. Arita, T. Koike, Y. Kayaki, T. Ikariya**
**Aerobic Oxidative Kinetic Resolution of Racemic Secondary Alcohols with Chiral Bifunctional Amido Complexes**

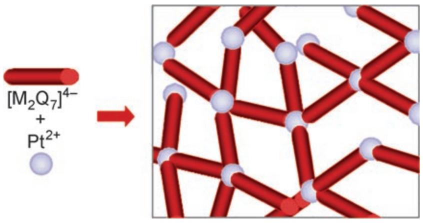
*T. Z. Forbes, J. G. McAlpin, R. Murphy, P. C. Burns**
**Metal–Oxygen Isopolyhedra Assembled into Fullerene Topologies**

## Obituary

## Books

## Highlights

### Porous Materials



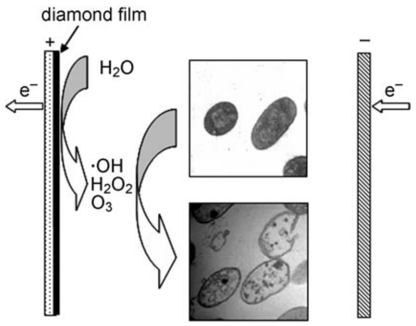
**Picking holes**: Self-assembly of germanium chalcogenide clusters in the presence of metal ions is a new and promising approach to the synthesis of porous semiconducting networks. Even monolithic highly porous aerogels with high internal surface areas can be prepared by sol–gel processing of anionic $[GeQ_4]^{4-}$, $[Sn_2Q_6]^{4-}$, or $[Ge_4Q_{10}]^{4-}$ clusters (Q = Se, S) in the presence of $Pt^{2+}$ (see scheme).

### Boron–Boron Double Bonds

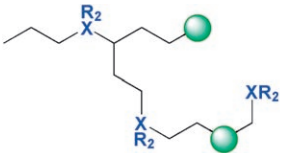
**The lightest double bond**, that is, the one between two atoms of boron, was finally realized in an electroneutral compound. Robinson et al. satisfied the electron demand of HB=BH through coordination of two molecules of an N-heterocyclic carbene (see scheme). As by-product, the base-stabilized parent diborane(4), the formal hydrogenation product of the title compound, was isolated.

## Minireviews

**"Water, water, everywhere, but not a drop to drink."** The most important step in the production of safe drinking water is the elimination of pathogenic microorganisms. Electrochemical systems with diamond films are promising alternatives to chlorination for disinfection of drinking water. As reactive oxygen species are generated in these systems (see picture), the formation of potentially toxic products such as chloroform from chlorine can be avoided.

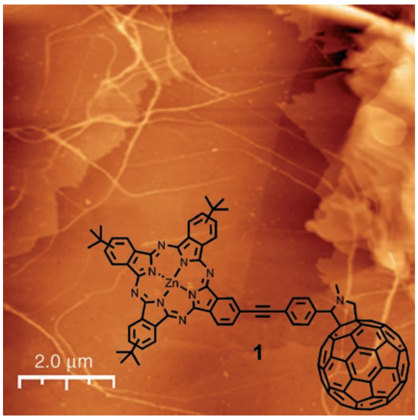


## Reviews



**Agents of change**: Chain-transfer processes are efficient and selective chemical means to achieve in situ functionalization of polyolefins in polymerization reactions catalyzed by d- and f-block metals (see picture, X = heteroatom). A variety of electron-poor and electron-rich chain-transfer agents, including silanes, boranes, alanes, phosphines, and amines, effect selective chain termination with concomitant carbon–heteroelement bond formation during single-site olefin-polymerization processes.

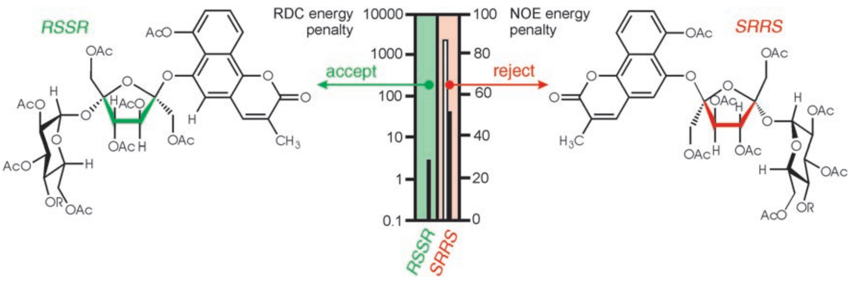
## Communications



**Conducting surfaces**: A covalently linked phthalocyanine–$C_{60}$ fullerene conjugate **1** (see picture) is able to self-organize on graphite and graphite-like surfaces, thus giving rise to supramolecular fibers and films. These nanostructures are electrically characterized by conductive atomic force microscopy and show outstanding nanoscale electrical conductivity.

**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.

## Glycoconjugates



**A new method** based on NMR spectroscopy is introduced to determine the absolute configuration of natural compounds and has been successfully applied to sucro-neolambertellin. The method relies on the measurement of residual dipolar couplings (RDCs), which allow the absolute configuration of unknown stereocenters to be related with known stereocenters (see picture). The approach is used to determine the configuration of the D-*threo*-2,5-hexodiulofuranose moiety by relating it to α-D-glucose.

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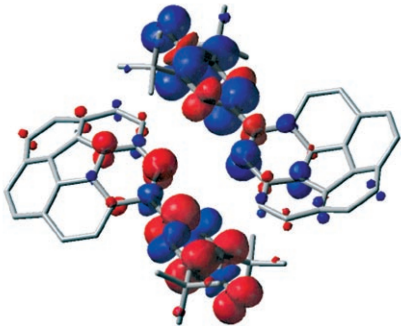
## Corannulene-Based Radicals



**A well-rounded radical**: A stable corannulene-based neutral radical with curved π conjugation was synthesized, and the crystal structure was determined. Unbalanced delocalized electronic spin on the three-dimensional π surface of the corannulene moiety (see spin-density distribution) demonstrates a sizable intermolecular exchange interaction and curved aromaticity.

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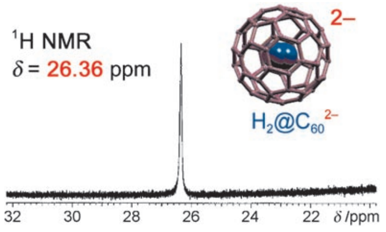
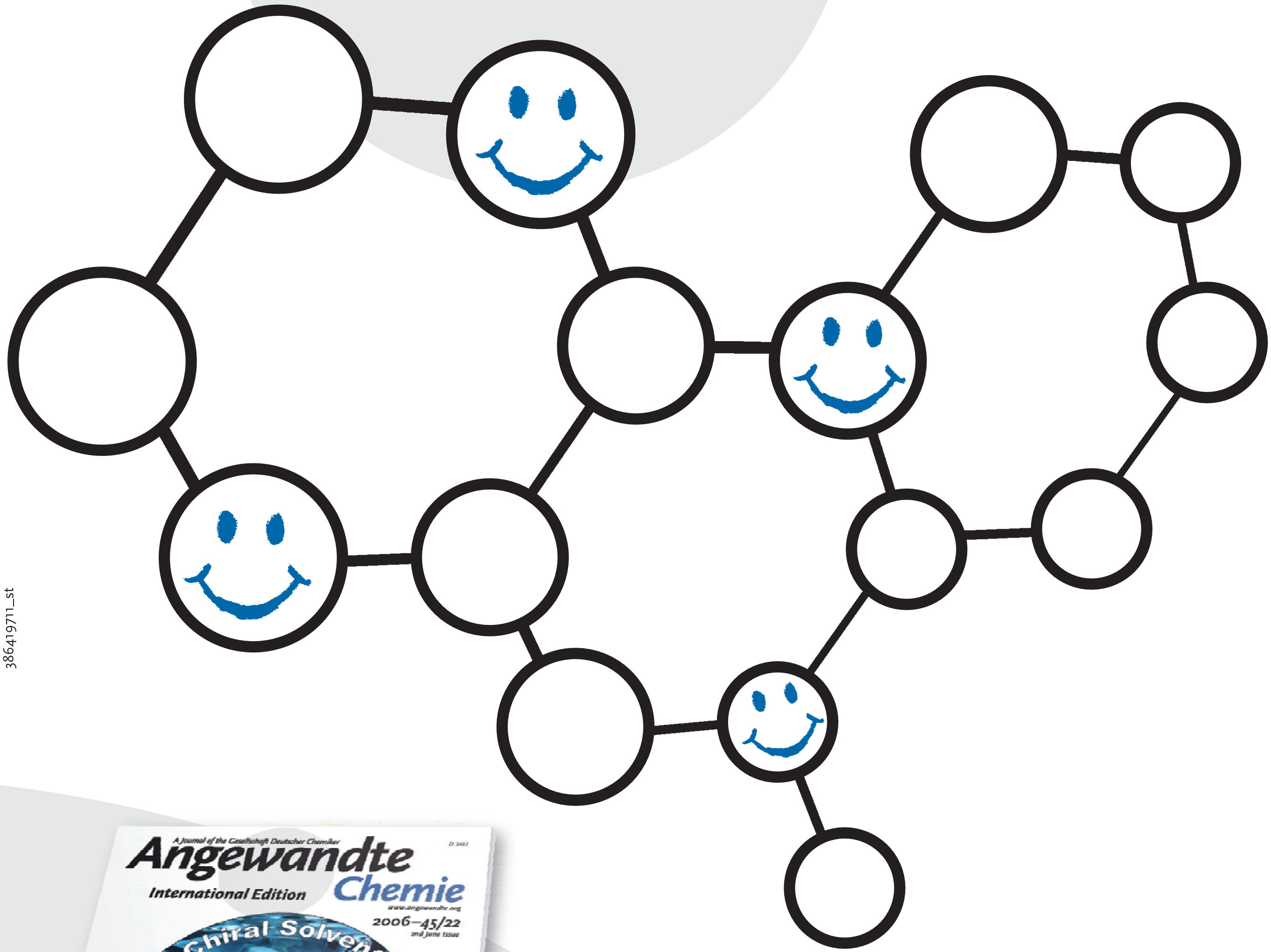
## Aromaticity

**Inside information**: The NMR signal of the molecular hydrogen in $H_2@C_{60}^{2-}$ appears at extraordinarily low field ($\delta = 26.36$ ppm) relative to that of neutral $H_2@C_{60}$. This can be explained by the decrease in aromaticity of the $C_{60}$ cage upon 2e reduction. Spherical delocalization of the added two electrons over the π system of the fullerene cage is thought to be responsible for the drastic change in fullerene aromaticity.



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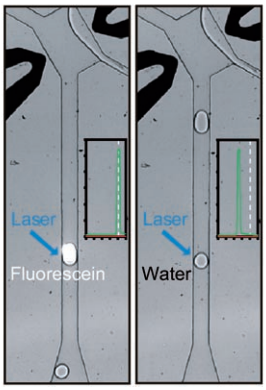
## Microfluidics

L. M. Fidalgo, G. Whyte, D. Bratton,
C. F. Kaminski, C. Abell,
W. T. S. Huck* **2042–2045**

From Microdroplets to Microfluidics: Selective Emulsion Separation in Microfluidic Devices



**The contents of microdroplets** can be extracted on-chip and incorporated by electrocoalescence into a continuous microfluidic stream. Individual droplets can be selected based on their contents. As a proof of principle, a fluorescence detection system was used to collect droplets containing low levels of a fluorescent dye (see picture of droplets passing through the device) as well as single fluorescent beads.

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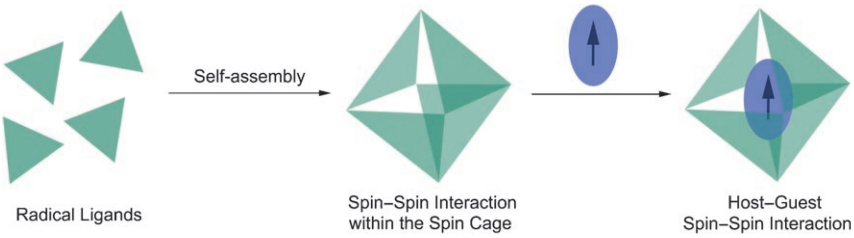
## Molecular Recognition

K. Nakabayashi, Y. Ozaki, M. Kawano,
M. Fujita* **2046–2048**

A Self-Assembled Spin Cage



**Going for a spin**: The quantitative self-assembly of a verdazyl radical-cored ligand with [Pd(bpy)$(NO_3)_2$] (bpy = 2,2′-bipyridyl) generates a large $M_6L_4$ spin cage in which multiple spin centers effectively surround the cavity. The inclusion of a radical guest within the cavity induces spin–spin interactions between the host and the guest.

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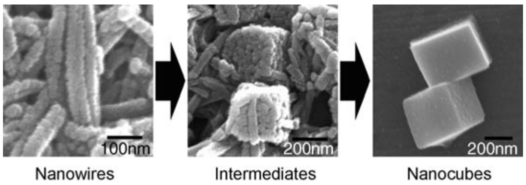
## Coordination Polymer Nanoparticles

S. Jung, M. Oh* **2049–2051**

Monitoring Shape Transformation from Nanowires to Nanocubes and Size-Controlled Formation of Coordination Polymer Particles



**Fluorescent CPPs** (coordination polymer particles) with controllable sizes ranging from the nano- to the microscale were synthesized in high yield by a solvothermal approach involving zinc ions and a carboxy-functionalized salen ligand. The initially formed nanowires aggregate to form cube-like clusters which undergo intrastructural fusion to produce uniform cubic particles, as shown by the depicted sequence of SEM images.

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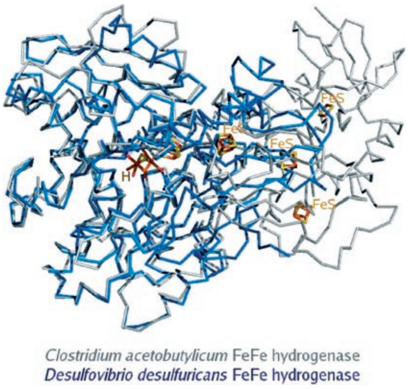
## Hydrogenases

C. Baffert, M. Demuez, L. Cournac,
B. Burlat, B. Guigliarelli, P. Bertrand,
L. Girbal, C. Léger* **2052–2054**

Hydrogen-Activating Enzymes: Activity Does Not Correlate with Oxygen Sensitivity

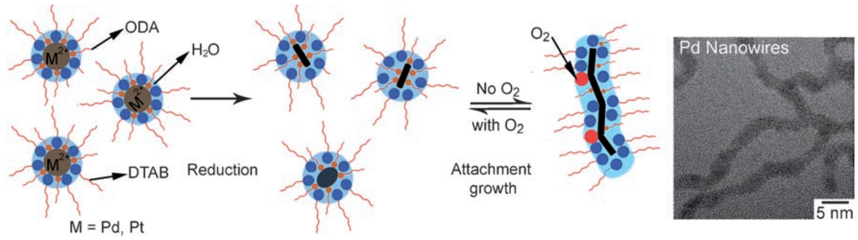


**Surprisingly uninhibited**: The inhibition of hydrogenases by oxygen is intensely studied because this is the main obstacle to using these enzymes in biofuel cells. The hydrogenase from *Clostridium acetobutylicum* (see structure) was found to react surprisingly slowly with $O_2$. The inhibition mechanism was elucidated and the kinetics were quantitatively defined. This is a prerequisite for improving the enzyme further by genetic engineering and for assessing its potential in technological devices.

## Metallic Nanowires

X. Teng, W.-Q. Han,* W. Ku,
M. Hücker ______ **2055 – 2058**

Synthesis of Ultrathin Palladium and Platinum Nanowires and a Study of Their Magnetic Properties

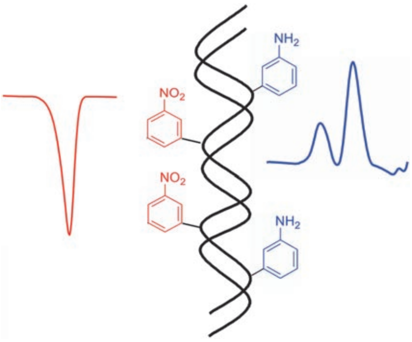


**Thin and wiry**: Ultrathin palladium and platinum nanowires with widths of 2.4 ± 0.2 (Pd) and 2.3 ± 0.2 nm (Pt) and lengths of over 30 nm are synthesized by a modified phase-transfer method (see picture). Both nanowires show ferromagnetic properties and unusual shifts in their hysteresis loops at low temperature. ODA = octadecylamine, DTAB = *n*-dodecyltrimethylammonium bromide.

## DNA Labeling

H. Cahová, L. Havran, P. Brázdilová,
H. Pivoňková, R. Pohl, M. Fojta,*
M. Hocek* ______ **2059 – 2062**

Aminophenyl- and Nitrophenyl-Labeled Nucleoside Triphosphates: Synthesis, Enzymatic Incorporation, and Electrochemical Detection



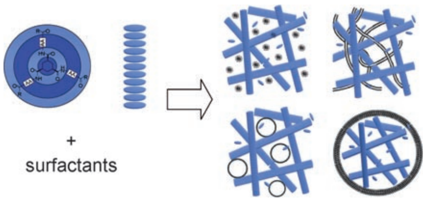
**Primer extension** is used to incorporate labeled nucleoside triphosphates into oligonucleotides (ONs). Aminophenyl and nitrophenyl modifications serve as electrochemical labels that are detectable by either oxidation or reduction, respectively (see representation of the ON double strand and redox curves). The redox potentials of the labels differ depending on the nucleobase and respond to incorporation into ONs.

## Self-Assembly

A. Brizard, M. Stuart, K. van Bommel,
A. Friggeri, M. de Jong,
J. van Esch* ______ **2063 – 2066**

Preparation of Nanostructures by Orthogonal Self-Assembly of Hydrogelators and Surfactants

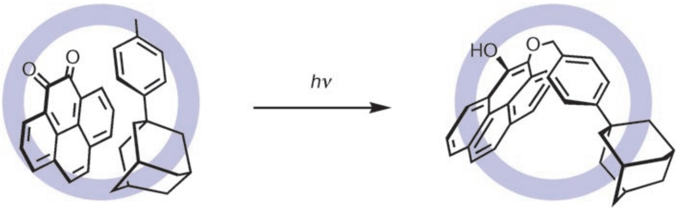
**Social networking**: A variety of novel multicompartment nanostructures has been easily formed by combining the supramolecular aggregative properties of surfactants with low-molecular-weight hydrogelators that are based on 1,3,5-cyclohexyltricarboxamide (see picture, AA = amino acid). The resulting structures include self-assembled interpenetrating networks.



## Host–Guest Systems

T. Yamaguchi, M. Fujita* ______ **2067 – 2069**

Highly Selective Photomediated 1,4-Radical Addition to *o*-Quinones Controlled by a Self-Assembled Cage



**Cavity control**: A highly selective 1,4-addition reaction of a toluene derivative to *o*-quinones proceeds efficiently within a self-assembled coordination cage (see scheme). The cage accelerates the formation of the 1,4-adduct but suppresses all other reaction pathways that are normally favorable in the absence of the cage.

## Supramolecular Chemistry

M. A. Alam, Y.-S. Kim, S. Ogawa, A. Tsuda,* N. Ishii, T. Aida* **2070–2073**

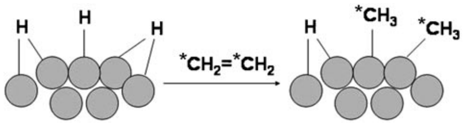
Directed 1D Assembly of a Ring-Shaped Inorganic Nanocluster Templated by an Organic Rigid-Rod Molecule: An Inorganic/Organic Polypseudorotaxane

**Facing up to matters**: Template-assisted cofacial assembly of a ring-shaped polyoxomolybdate cluster (MC) by an oligomeric *p*-phenylenebutadiynylene rigid rod molecule bearing ammonium ion pendant groups ($PB_n$) allowed for the formation of an inorganic/organic one-dimensional (1D) nanoobject. Studies indicate that the 1D object most likely has a polypseudorotaxane structure (see picture), in which multiple MC rings are threaded by the $PB_n$ rod.

## Surface Chemistry

J. García-Antón, M. R. Axet, S. Jansat, K. Philippot, B. Chaudret,* T. Pery, G. Buntkowsky, H.-H. Limbach **2074–2078**

Reactions of Olefins with Ruthenium Hydride Nanoparticles: NMR Characterization, Hydride Titration, and Room-Temperature C–C Bond Activation

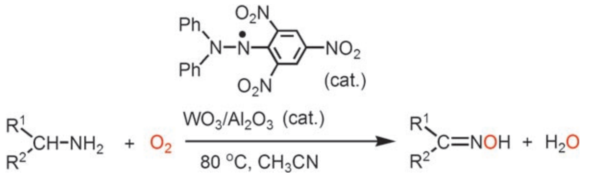


**Surface C–C bond activation**: Ruthenium nanoparticles prepared by hydrogenation of an organometallic precursor accommodate more than one hydride per surface ruthenium atom as well as various ligands, such as amines or phosphines, as shown by gas-phase, liquid, and solid-state NMR spectroscopy and titration with olefins. These nanoparticles react with ethylene at room temperature to give ethane and surface-bound methyl species (see scheme).

## Aerobic Catalytic Oxidation

K. Suzuki,* T. Watanabe, S.-I. Murahashi* **2079–2081**

Aerobic Oxidation of Primary Amines to Oximes Catalyzed by DPPH and $WO_3/Al_2O_3$

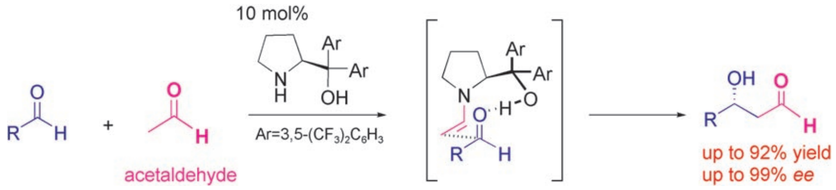


**Catalytic teamwork**: Aerobic oxidation of primary amines to the corresponding oximes proceeds highly efficiently in the presence of the catalysts 1,1-diphenyl-2-picrylhydrazyl (DPPH) and $WO_3/Al_2O_3$ under mild conditions (see scheme). This new method is both selective and environmentally benign.

## Organocatalysis

Y. Hayashi,* T. Itoh, S. Aratake, H. Ishikawa **2082–2084**

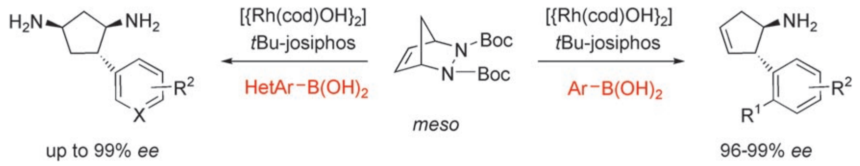
A Diarylprolinol in an Asymmetric, Catalytic, and Direct Crossed-Aldol Reaction of Acetaldehyde



**No over-reacting**: A diarylprolinol was found to be an effective organocatalyst of the direct, enantioselective aldol reaction of acetaldehyde, affording β-hydroxy α-unsubstituted aldehydes in good yield with excellent enantioselectivity (see scheme). In the proposed transition state the aldehyde reacts on the more hindered face of the intermediate enamine as a consequence of the hydrogen bond between the aldehyde and the OH group of the organocatalyst.

# Contents

### Asymmetric Catalysis



**Divergent bicycle paths**: A chemodivergent desymmetrization occurs after an initial enantioselective carbometalation step. The reaction brings a solution to the challenging problem of the enantioselective ring-opening of diazabicyclo[2.2.1]heptanes to obtain arylated cyclopentenamines (see scheme, right). An alternative reaction pathway was discovered in which C−H insertion/1,4-metal migration occurs to give reductive arylation products (left).

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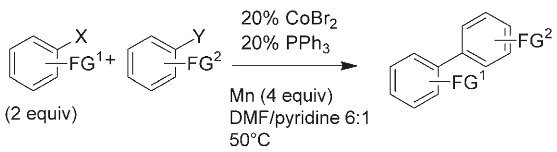
### C−C Coupling



**No prior preparation** of the organometallic reagent is required in a cobalt-catalyzed coupling of two different aryl halides under mild conditions (see scheme). A broad spectrum of valuable biaryl compounds can be prepared in this way. Not only may a variety of reactive substituents be present, but heteroaryl halides and aryl triflates are also suitable substrates. DMF = *N*,*N*-dimethylformamide, FG = functional group.

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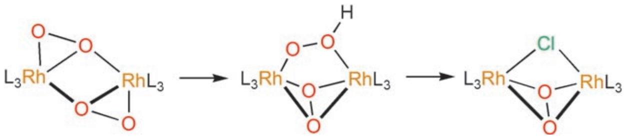
### Stable Hydroperoxido Complex



**A novel coordination mode** of the hydroperoxido ligand in which each oxygen atom is bonded to a distinct metal center is present in a rare thermally stable example of this otherwise elusive family of complexes, which was obtained by protonating a bis-peroxido-bridged Rh$_2$ complex. The OOH ligand is displaced by a chloride ion to give the corresponding chlorido-bridged complex (see scheme, L$_3$ = tris(methylenediphenylphosphane)-phenylborate).

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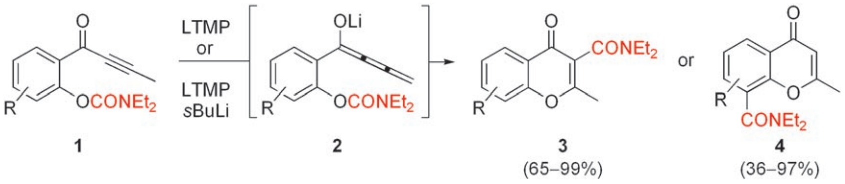
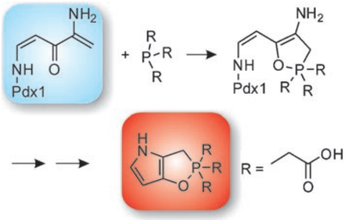
### Synthetic Methods



**Completing the circle**: A synthesis of chromone 3- and 8-carboxamides (**3** and **4**) from 2-but-2-ynoyl aryl *O*-carbamates **1** has been achieved via common intermediate **2** in a regioselective manner. Repetitive metalation reactions and an iridium-catalyzed B$_2$pin$_2$ borylation lead to the construction of polysubstituted chromones, which are key components of many bioactive compounds.



**$I_{320}$ has it**: The serendipitous trapping, by aromatization, of an enzyme-bound chromophoric intermediate ($I_{320}$; see picture, blue box) involved in vitamin $B_6$ formation using a common biological reducing agent provides new information regarding the structure of the chromophoric species.

## Trapping Reactions

J. W. Hanes, I. Keresztes,
T. P. Begley* ______ **2102–2105**

Trapping of a Chromophoric Intermediate in the Pdx1-Catalyzed Biosynthesis of Pyridoxal 5′-Phosphate

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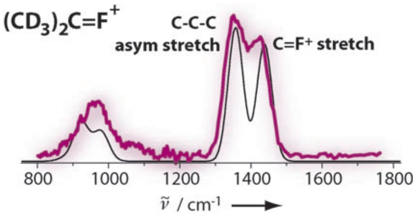
**The gaseous ion $(CD_3)_2CF^+$**, which is isoelectronic with acetone, has a stretching vibration in the resonant IR multiphoton dissociation (IRMPD) spectrum, indicating a high degree of double-bond character in the C–F bond (see picture). Absorption bands predicted by density functional calculations with anharmonic corrections (black line) agree well with the experimental spectrum.



## C=F$^+$ Stretching

J. Oomens, T. H. Morton* ______ **2106–2108**

The Cationic C=F$^+$ Stretching Vibration in the Gas Phase

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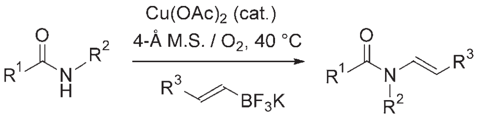

**A new partner**: Potassium alkenyltrifluoroborate salts undergo coupling with amides to give enamides in the presence of a $Cu(OAc)_2$ catalyst and under mild oxidative conditions (see scheme). The air- and water-stable alkenyltrifluoroborate salts offer a convenient alternative to alkenyl halides as cross-coupling partners. A range of amides undergo coupling including cyclic amides, imides, and carbamates as well as benzamides.

## Copper Catalysis

Y. Bolshan, R. A. Batey* ______ **2109–2112**

Enamide Synthesis by Copper-Catalyzed Cross-Coupling of Amides and Potassium Alkenyltrifluoroborate Salts

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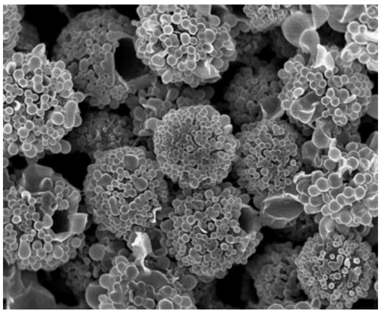
**Blooming block copolymers!** Uniform droplets of solvent that contain amphiphilic polystyrene–poly(ethylene oxide) diblock copolymers are prepared using a microcapillary device. Solvent removal drives interfacial instabilities, through which the polymer assembles into complex hierarchical microparticle structures (see picture).



## Microparticles

J. T. Zhu, R. C. Hayward* ______ **2113–2116**

Hierarchically Structured Microparticles Formed by Interfacial Instabilities of Emulsion Droplets Containing Amphiphilic Block Copolymers

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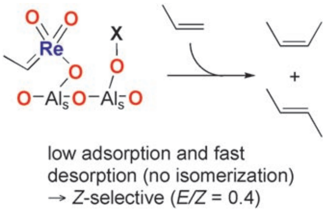


**Supported metathesis**: Grafting $(CH_3)ReO_3$ onto alumina covered with surface trimethylsilyl groups increases the efficiency and selectivity of this catalyst in olefin metathesis (see scheme). The $SiMe_3$ groups (X) modify the adsorption properties of alumina by favoring desorption and thereby disfavoring secondary reactions.

## Olefin Metathesis

A. Salameh, A. Baudouin, J.-M. Basset,
C. Copéret* ______ **2117–2120**

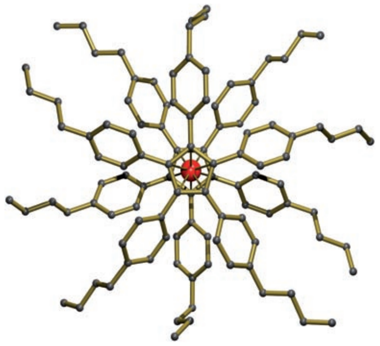
Tuning the Selectivity of Alumina-Supported $(CH_3)ReO_3$ by Modifying the Surface Properties of the Support

## Cyclopentadienyl Complexes

C. Ruspic, J. R. Moss, M. Schürmann, S. Harder* ______ 2121 – 2126

### Remarkable Stability of Metallocenes with Superbulky Ligands: Spontaneous Reduction of Sm$^{III}$ to Sm$^{II}$

**Unexpected attraction** between extremely bulky cyclopentadienyl ligands of opposite chirality has been observed in perarylated metallocenes $[(Ar_5C_5)_2M]$. The exceptional stability of such sterically congested metallocenes (see structure) is explained by a merry-go-round C–H···C(π) hydrogen-bond network. This stabilizing force even enables spontaneous reduction of a Sm$^{III}$ precursor to a Sm$^{II}$ metallocene.



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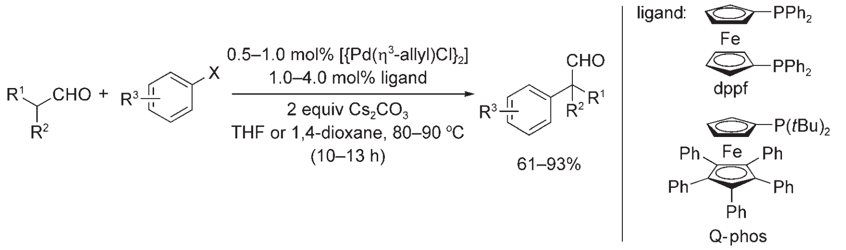
## α-Arylation of Aldehydes

G. D. Vo, J. F. Hartwig* ______ 2127 – 2130

### Palladium-Catalyzed α-Arylation of Aldehydes with Bromo- and Chloroarenes Catalyzed by $[\{Pd(allyl)Cl\}_2]$ and dppf or Q-phos



**Pd source matters**: A general method for palladium-catalyzed α-arylation of aldehydes (see scheme) was developed to couple linear and branched aldehydes with electron-poor and electron-rich bromo- and chloroarenes.

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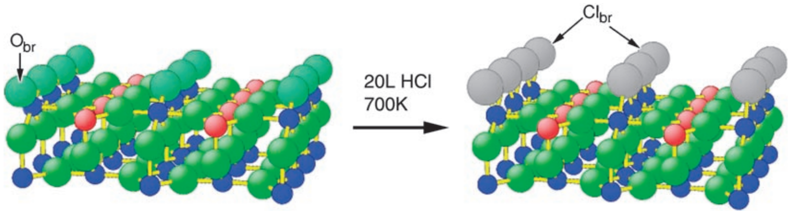
## Surface Chemistry

D. Crihan, M. Knapp, S. Zweidinger, E. Lundgren, C. J. Weststrate, J. N. Andersen, A. P. Seitsonen, H. Over* ______ 2131 – 2134

### Stable Deacon Process for HCl Oxidation over RuO$_2$



**Selective substitution**: In the oxidation of HCl with oxygen to give Cl$_2$ and water, RuO$_2$(110) serves as a stable, active model catalyst for the Sumitomo process (see picture; Ru in red and blue). The stability of the catalyst is related to the selective replacement of undercoordinated bridging surface O atoms (O$_{br}$) by Cl atoms (Cl$_{br}$). The chlorination of RuO$_2$(110) is self-limiting, in that chlorine incorporation terminates when all bridging O atoms are replaced.

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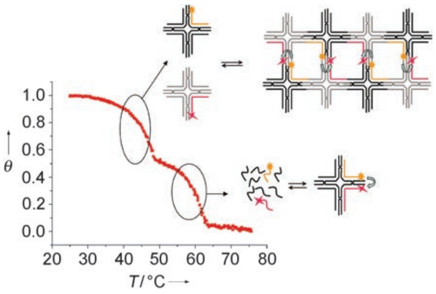
## DNA Nanostructures

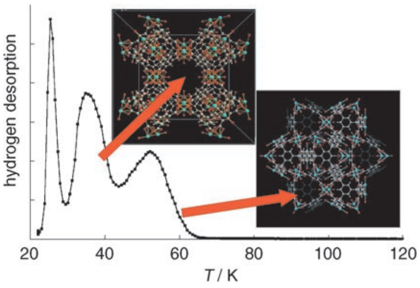
B. Saccà,* R. Meyer, U. Feldkamp, H. Schroeder, C. M. Niemeyer* ______ 2135 – 2137

### High-Throughput, Real-Time Monitoring of the Self-Assembly of DNA Nanostructures by FRET Spectroscopy



**Tiles and arrays**: The self-assembly of DNA nanostructures can be monitored in real time and with high throughput by FRET spectroscopy. A van't Hoff analysis of the fluorescence data allows for a complete thermodynamic characterization of the tile formation as well as array formation (see picture).

### Hydrogen Storage



**The diameter is decisive**: Adsorption sites for hydrogen in the metal–organic frameworks Cu-BTC, MIL-53, MOF-5, and IRMOF-8 could be identified by using thermal desorption spectroscopy at very low temperatures (see graph). The correlation between the desorption spectra and the pore structure of these MOFs shows that at high hydrogen concentrations the diameter of the cavity determines the heat of adsorption.

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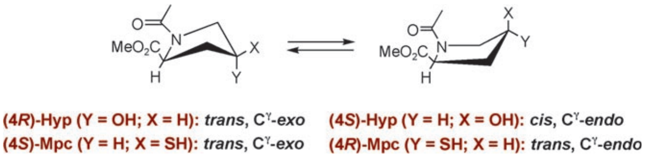
### Proline Conformations



**Spot the difference**: Conformational analysis of the 2*S*,4*R* and 2*S*,4*S* epimers of *N*-acetyl-4-mercaptopyrrolidine-2-carboxylic acid methyl esters reveals ring-pucker preferences that are opposite of those of the hydroxyproline derivatives (see scheme). Replacement of proline or hydroxyproline in polypeptides with the chalcogen analogue should allow for fine-tuning of the complex interplay of non-covalent interactions, steric hindrance, and stereoelectronic effects.

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

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

## Service

# Corrigenda

### Regioselective Aliphatic Retro-[1,4]-Brook Rearrangements

Y. Mori,* Y. Futamura,
K. Horisaki ____________ **1091–1093**

*Angew. Chem. Int. Ed.* **2008**, *47*

DOI 10.1002/anie.200702539

The citation in the third last sentence of the first paragraph of this Communication was incorrect. The correct citation is given below. The authors apologize for this oversight. "It has recently been reported that the regioselectivity of the retro-[1,2]- and [1,4]-Brook rearrangements in an allyllithium system depends upon the reaction conditions, and that the addition of hexamethylphosphoramide (HMPA) as a cosolvent improves the [1,4] selectivity.[5n]"

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[5] n) A. Nakazaki, T. Nakai, K. Tomooka, *Angew. Chem.* **2006**, *118*, 2293 – 2296; *Angew. Chem. Int. Ed.* **2006**, *45*, 2235 – 2238.

### Enantiomerically Enriched Cyclopropene Derivatives: Versatile Building Blocks in Asymmetric Synthesis

I. Marek,* S. Simaan,
A. Masarwa ____________ **7364–7376**

*Angew. Chem. Int. Ed.* **2007**, *46*

DOI 10.1002/anie.200604774

The authors of this Review wish to clarify that, although, as reported, the first asymmetric synthesis of chiral cyclopropene derivatives was jointly reported by Doyle, Müller, and co-workers in 1992,[1] the first example of a chiral cyclopropene was obtained by resolution in 1968 by Breslow and Douek.[2]

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[1] M. N. Protopopova, M. P. Doyle, P. Müller, D. Ene, *J. Am. Chem. Soc.* **1992**, *114*, 2755.
[2] R. Breslow, M. Douek, *J. Am. Chem. Soc.* **1968**, *90*, 2698.