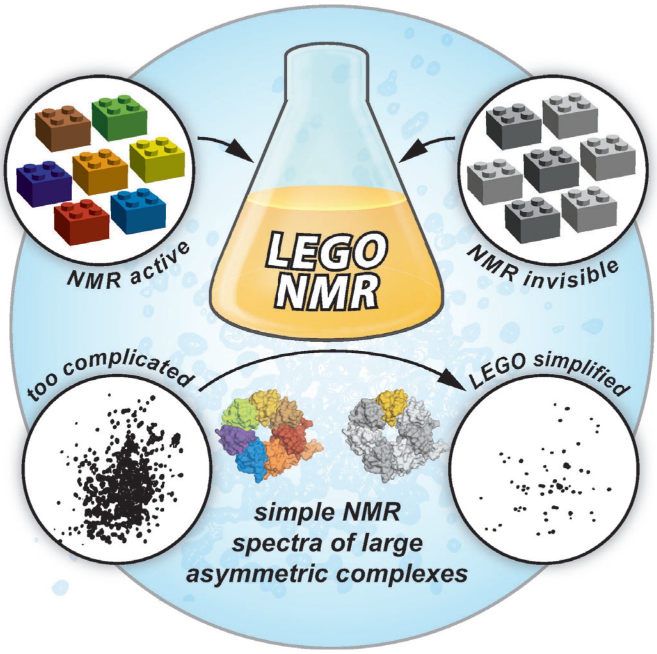
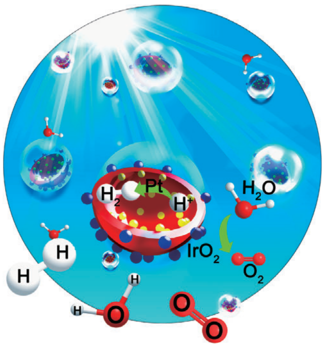
Large asymmetric assemblies ...

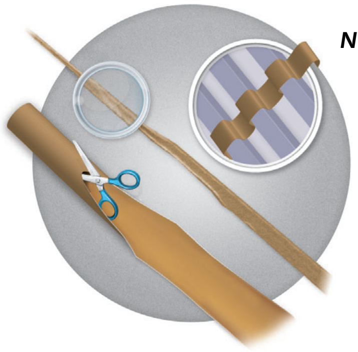


… are difficult to prepare recombinantly and result in complicated NMR spectra that cannot be analyzed in detail. Both issues are addressed simultaneously in the LEGO-NMR method described by R. Sprangers and co-workers in their Communication on page 11401 ff. The method is based on sequential co-expression of NMR active and NMR invisible protein subunits of a large assembly and significantly simplifies both amide backbone and methyl side-chain spectra.



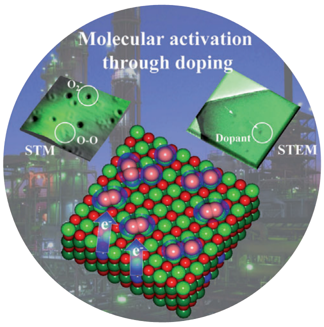
Water Splitting

In their Communication on page 11252 ff., K. Domen et al. present a simple method for the preparation of core–shell photocatalysts with spatially separated co-catalysts for efficient water splitting.



Nanostructures

Crystalline semiconductor nanoribbons are obtained by unwrapping core–shell nanowires, as described by F. Patolsky et al. in their Communication on page 11298 ff. An example for such an accessible material is technologically important germanium nanoribbon structures.



Oxygen Activation

In their Communication on page 11395 ff., N. Nilius et al. report that chemically inert Mo-doped CaO films activate adsorbed O_2 by charge transfer. The resulting oxygen surface species then dissociate as atomic oxygen.

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Spotlight on Angewandte's Sister Journals — *11194 – 11196*

Author Profile

"My favorite food is sashimi and Peking duck. If I were not a scientist, I would be a security guard for the National Parks of Taiwan …"
This and more about Rai-Shung Liu can be found on page 11406.

Rai-Shung Liu — **11198**

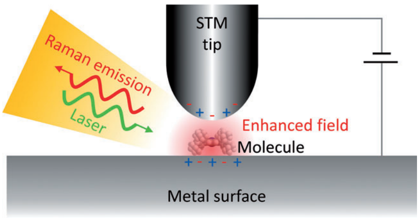
Books

Nanomaterials in Catalysis — Philippe Serp, Karine Philippot — *reviewed by V. Polshettiwar* — **11199**

Highlights

Single-Molecule Spectroscopy

Tip-enhanced Raman spectroscopy combines scanning probe techniques with Raman spectroscopy. Latest developments permit the chemical mapping of individual adsorbed molecules by monitoring molecular vibrations with subnanometer resolution. Increased efficiency and reduced photodegradation make this method suitable for studies of adsorbed organic and biomolecules in surface science, catalysis, biochemistry, and related fields.



J. M. Gottfried* — **11202 – 11204**

Where Does It Vibrate? Raman Spectromicroscopy on a Single Molecule

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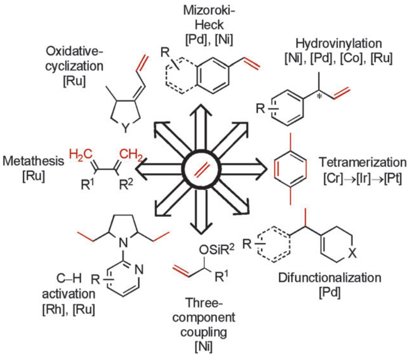
Minireviews

Synthetic Methods

V. Saini, B. J. Stokes,
M. S. Sigman* ________ **11206 – 11220**

Transition-Metal-Catalyzed Laboratory-Scale Carbon–Carbon Bond-Forming Reactions of Ethylene



Functionalize or be functionalized: Ethylene is a valuable reactant for the transition-metal-catalyzed synthesis of a variety of useful small molecules. Examples of some of the latest carbon–carbon bond-forming methods are described, many of which are carried out at ambient temperature and pressure. The outcome is often the incorporation of a synthetically versatile vinyl functional group.

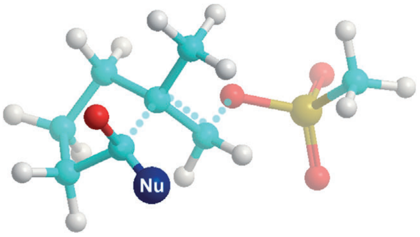
Reviews

Heterolytic Fragmentation

M. A. Drahl, M. Manpadi,
L. J. Williams* ________ **11222 – 11251**

C–C Fragmentation: Origins and Recent Applications

It has been sixty years since Eschenmoser and Frey disclosed the archetypal C–C fragmentation reaction. New fragmentation reactions that give alkynes and allenes, and variants of the original, have been invented and applied to many complex motifs and natural products.



Communications

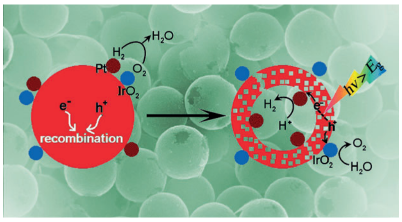
Photocatalysis

D. Wang, T. Hisatomi, T. Takata, C. Pan,
M. Katayama, J. Kubota,
K. Domen* ________ **11252 – 11256**

Core/Shell Photocatalyst with Spatially Separated Co-Catalysts for Efficient Reduction and Oxidation of Water

Frontispiece

A simple method allows the preparation of core/shell photocatalysts with spatially separated co-catalysts for efficient water splitting. The high activity was attributed to the core/shell structure and separated co-catalysts that assisted separation and collection of the electrons and holes at the respective co-catalysts, owing to active rectification of electron and hole transport (see picture; $E_g = 2.1$ eV).



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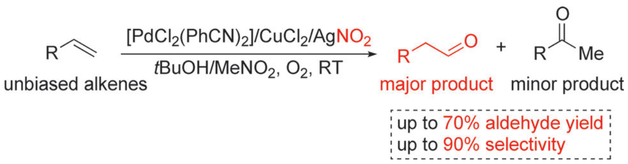
Synthetic Methods

Z. K. Wickens, B. Morandi,
R. H. Grubbs* ________ 11257 – 11260

Aldehyde-Selective Wacker-Type Oxidation of Unbiased Alkenes Enabled by a Nitrite Co-Catalyst

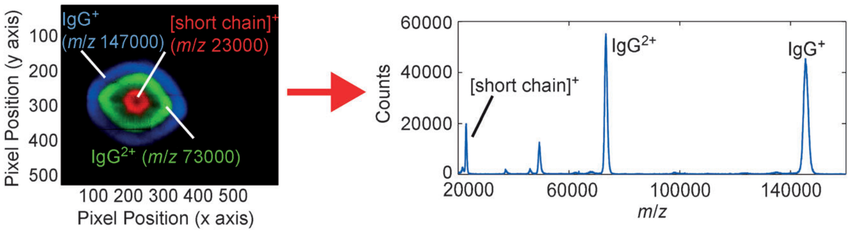


Breaking the rules: Reversal of the high Markovnikov selectivity of Wacker-type oxidations was accomplished using a nitrite co-catalyst. Unbiased aliphatic alkenes can be oxidized with high yield and aldehyde selectivity, and several functional groups are tolerated. ^{18}O-labeling experiments indicate that the aldehydic O atom is derived from the nitrite salt.

Mass Spectrometry

S. R. Ellis, J. H. Jungmann, D. F. Smith,
J. Soltwisch,
R. M. A. Heeren* ________ 11261 – 11264

Enhanced Detection of High-Mass Proteins by Using an Active Pixel Detector

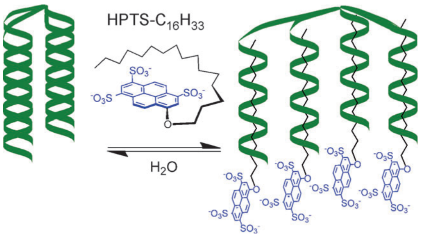


Flying high: Application of an active pixel detector with high charge sensitivity to a linear time-of-flight mass spectrometer results in enhanced detection of high-mass proteins (such as Immunoglobulin G; IgG) using a conventional microchannel plate detection system. This technique thus provides a means to extend the mass range of such detectors as well as allowing direct visualization of mass-dependent ion-focusing phenomena (see picture).

Polysaccharide Branching

S. R. Beeren,*
O. Hindsgaul* ________ 11265 – 11268

Nature's Dendrimer: Characterizing Amylopectin as a Multivalent Host

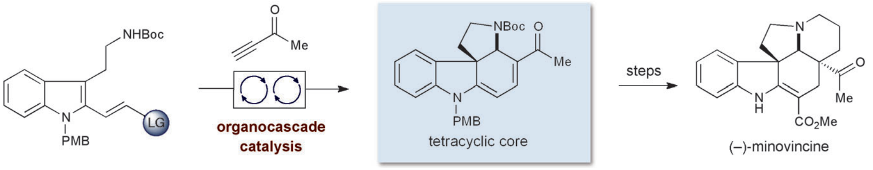


Hang on to those branches! Amylopectin, the major polysaccharide of starch, is a predominantly α(1,4)-linked glucan whose properties are defined by its size and the number, distribution, and length of its α(1,6)-linked branches. The amphiphilic probe HPTS-$C_{16}H_{33}$ binds to terminal helical branches longer than 12 glucose units (green), which allows for a detailed quantitative characterization of polysaccharide branching by ^{1}H NMR spectroscopy.

Natural Product Synthesis

B. N. Laforteza, M. Pickworth,
D. W. C. MacMillan* ________ 11269 – 11272

Enantioselective Total Synthesis of (−)-Minovincine in Nine Chemical Steps: An Approach to Ketone Activation in Cascade Catalysis



Dressed to the nines: The first enantioselective total synthesis of (−)-minovincine has been accomplished in nine chemical steps and 13% overall yield. A novel, one-step Diels–Alder/β-elimination/conjugate addition organocascade sequence allowed rapid access to the central tetracyclic core in an asymmetric manner. Boc = *tert*-butoxycarbonyl, LG = leaving group, PMB = *para*-methoxybenzyl.

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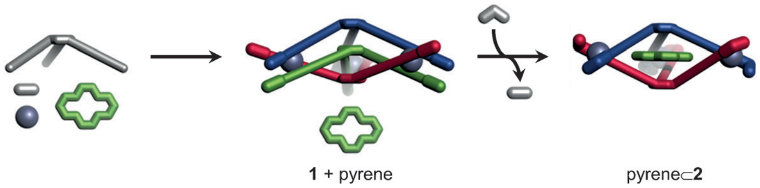
Systems Chemistry

A. Sørensen, A. M. Castilla, T. K. Ronson, M. Pittelkow, J. R. Nitschke* 11273 – 11277

Chemical Signals Turn On Guest Binding through Structural Reconfiguration of Triangular Helicates



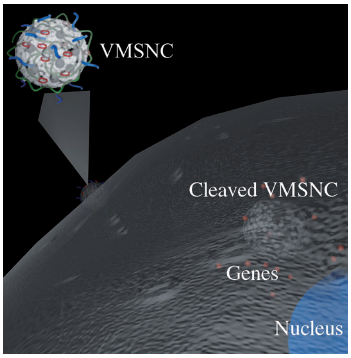
Be my guest: The function of a system based on self-assembled Zn^{II} complexes can be controlled by external chemical stimuli. The complexes are based on a C_3-symmetric ligand that forms a unique triangular triple helicate structure **1**. Upon subcomponent substitution, **1** is able to transform into a triangular double helicate **2** which, unlike **1**, can encapsulate guests.

Virus-Mimetic Gene Transfer

N. Gandra, D. Wang, Y. Zhu, C. B. Mao* 11278 – 11281

Virus-Mimetic Cytoplasm-Cleavable Magnetic/Silica Nanoclusters for Enhanced Gene Delivery to Mesenchymal Stem Cells

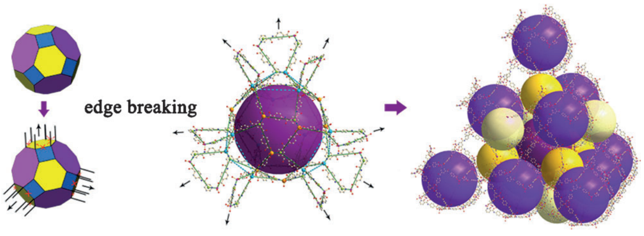
It does get in: Phage is made of DNA as a core and protein as a coat, and it can transfer DNA into host cells with high efficiency. Phage-mimetic gene transfer to hard-to-transfect mesenchymal stem cells (MSCs) was achieved using virus-mimetic magnetic silica nanoclusters (VMSNCs). The VMSNCs bear MSC-homing phage-borne protein on the surface and encapsulate DNA inside, promoting the transfer of DNA into MSCs.



Metal–Organic Frameworks

R. R. Yun, Z. Y. Lu, Y. Pan, X.-Z. You, J. Bai* 11282 – 11285

Formation of a Metal–Organic Framework with High Surface Area and Gas Uptake by Breaking Edges Off Truncated Cuboctahedral Cages



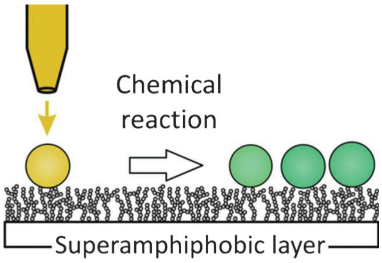
Breaking edges off regular truncated cuboctahedra leads to a metal–organic framework (MOF) with polybenzene topology. This fully characterized MOF with lowest connectivity has the largest BET surface area among interpenetrated MOFs.

Microparticles

X. Deng, M. Paven, P. Papadopoulos, M. Ye, S. Wu, T. Schuster, M. Klapper, D. Vollmer,* H.-J. Butt* 11286 – 11289

Solvent-Free Synthesis of Microparticles on Superamphiphobic Surfaces

Polymeric and composite microspheres can be synthesized without solvents or process liquids by using superamphiphobic surfaces. In this method, the repellency of superamphiphobic layers to monomers and polymer melts and the extremely low adhesion to particles are taken advantage of.



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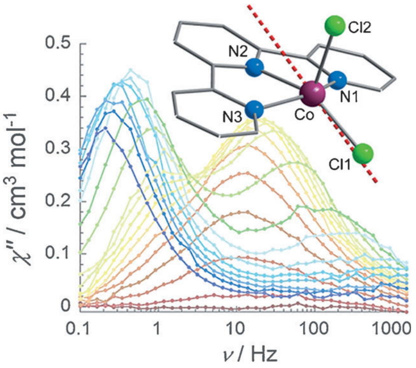
Single-Molecule Magnets

F. Habib, O. R. Luca, V. Vieru, M. Shiddiq, I. Korobkov, S. I. Gorelsky, M. K. Takase, L. F. Chibotaru, S. Hill, R. H. Crabtree, M. Murugesu* ________ **11290 – 11293**

Influence of the Ligand Field on Slow Magnetization Relaxation versus Spin Crossover in Mononuclear Cobalt Complexes

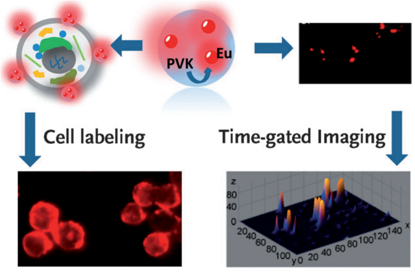
The electronic and magnetic properties of the complexes [Co(terpy)Cl_2] (**1**), [Co(terpy)$(NCS)_2$] (**2**), and [Co$(terpy)_2$]$(NCS)_2$ (**3**) were investigated. The coordination environment around Co^{II} in **1** and **2** leads to a high-spin complex at low temperature and single-molecule magnet properties with multiple relaxation pathways. Changing the ligand field and geometry with an additional terpy ligand leads to spin-crossover behavior in **3** with a gradual transition from high spin to low spin.



Fluorescence Imaging

W. Sun, J. B. Yu, R. P. Deng, Y. Rong, B. Fujimoto, C. F. Wu, H. J. Zhang, D. T. Chiu* ________ **11294 – 11297**

Semiconducting Polymer Dots Doped with Europium Complexes Showing Ultranarrow Emission and Long Luminescence Lifetime for Time-Gated Cellular Imaging



Bright dots: Semiconducting polymer dots (Pdots) doped with europium complexes possess line-like fluorescence emission, high quantum yield, and long fluorescence lifetime. The Pdots successfully labeled receptors on cells. The long fluorescence lifetime of the Pdots was used to distinguish them from other red fluorescence emitting nanoparticles, and improve the signal-to-noise ratio for time-gated cellular imaging. PVK = poly(9-vinylcarbazole).

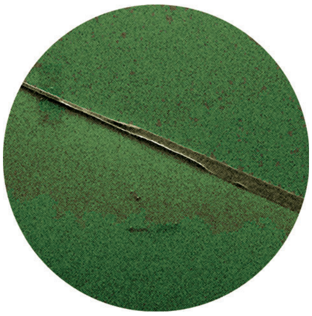
Nanostructures

A. Pevzner, G. Davidi, H. Peretz-Soroka, E. Havivi, Z. Barkay, R. Popovitz-Biro, A. Khatchtourints, F. Patolsky* ________ **11298 – 11302**

Unwrapping Core–Shell Nanowires into Nanoribbon-Based Superstructures

Inside Back Cover

A prize for the ribbons: High-quality crystalline semiconducting nanoribbons can be prepared by "unwrapping" core–shell nanowire precursors. For example, Ge nanowires were coated with a Si shell and the top surface was carved by etching whereas the sides were protected by a thin layer of photoresist material. Finally the Ge core was removed selectively by chemical means to give fully opened and flat nanoribbon structures (see picture).

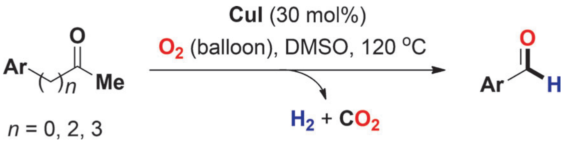


C–C Bond Cleavage

L. Zhang, X. Bi,* X. Guan, X. Li, Q. Liu,* B.-D. Barry, P. Liao ________ **11303 – 11307**

Chemoselective Oxidative C(CO)–C(methyl) Bond Cleavage of Methyl Ketones to Aldehydes Catalyzed by CuI with Molecular Oxygen

Inside Cover



Aldehyde Termination: A novel copper-catalyzed transformation from methyl ketones into aldehydes has been accomplished. This method is applicable to a wide range of aromatic and aliphatic methyl ketones and chemoselectively produces aldehydes, accompanied by the release of hydrogen (H_2) and carbon dioxide (CO_2) as by-products.

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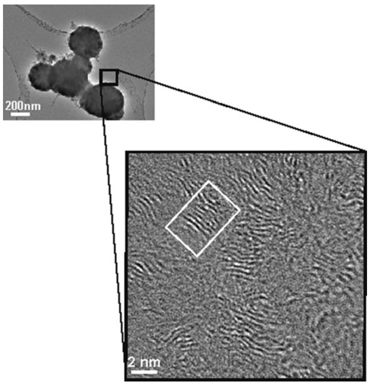
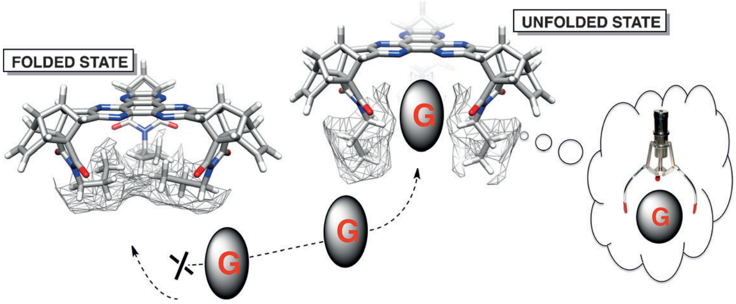


The shorter, the more dispersible: An iterative, emulsion-based shortening technique has been used to reduce the length of single-walled carbon nanotubes (SWNTs) to the same order of magnitude as their diameter (ca. 1 nm), thus achieving an effectively "zero-dimensional" structure with improved dispersibility and, after hydroxylation, long-term water solubility. Finally, zero-dimensional SWNTs were positively identified using mass spectrometry for the first time.

Carbon Nanotubes

K. Kamalasanan, R. Gottardi, S. Tan, Y. Chen, B. Godugu, S. Rothstein, A. C. Balazs, A. Star, S. R. Little* ______ **11308 – 11312**

"Zero-Dimensional" Single-Walled Carbon Nanotubes

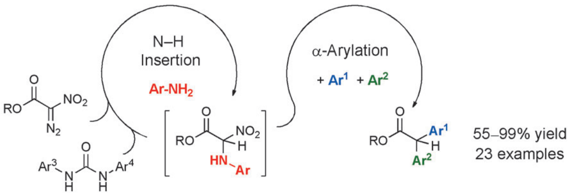


Up for grabs: A modular receptor comprises a hexaazatriphenylene "platform" and three imide residues on its concave side carrying flexible alkane chains. The chains not only populate the host's cavity but can also extend and can grab an appropriately sized and shaped guest in solution.

Dynamic Hosts

K. Hermann, M. Nakhla, J. Gallucci, E. Dalkilic, A. Dastan, J. D. Badjić* ______ **11313 – 11316**

A Molecular Claw: A Dynamic Cavitand Host



It takes two: A unique organocatalyzed cascade for the unsymmetric double arylation of α-nitrodiazoesters is described. This organocascade features the strategic use of carbene-activating anilines in conjunction with a urea catalyst, thus allowing for the synthesis of pharmaceutically attractive α-diarylesters through a transient N–H insertion process.

Organocatalysis

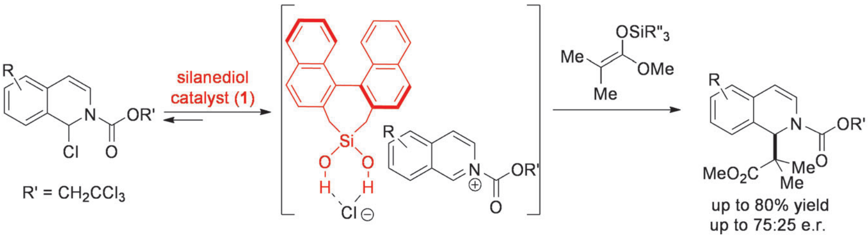
T. J. Auvil, S. S. So, A. E. Mattson* ______ **11317 – 11320**

Arylation of Diazoesters by a Transient N–H Insertion Organocascade

Organocatalysis

A. G. Schafer, J. M. Wieting, T. J. Fisher, A. E. Mattson* ———— **11321–11324**

Chiral Silanediols in Anion-Binding Catalysis

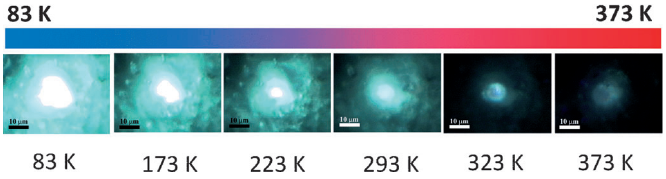


A perfect pair: Silanediols are effective catalysts for the addition of silyl ketene acetals to *N*-acylisoquinolinium ions. Importantly, this is the first example of a silanediol plausibly participating in anion-binding catalysis, a relatively new direction in the field of hydrogen-bond-donor catalysis. The chiral, enantiopure C_2-symmetric silanediol **1** catalyzes enantioselective transformations.

Non-contact Thermometry

S. L. Shinde, K. K. Nanda* ———— **11325–11328**

Wide-Range Temperature Sensing using Highly Sensitive Green-Luminescent ZnO and PMMA-ZnO Film as a Non-Contact Optical Probe

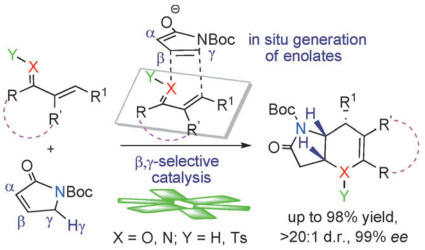


The heat is on: A variation of green luminescence intensity of ZnO microcrystals embedded in poly(methyl methacrylate) is observed. This material is used for non-contact thermometer, which has an accuracy of 0.1 K over a temperature range of 83–474 K. Scale bars: 10 µm.

Synthetic Methods

X. Jiang,* L. Liu, P. Zhang, Y. Zhong, R. Wang* ———— **11329–11333**

Catalytic Asymmetric β,γ Activation of α,β-Unsaturated γ-Butyrolactams: Direct Approach to β,γ-Functionalized Dihydropyranopyrrolidin-2-ones

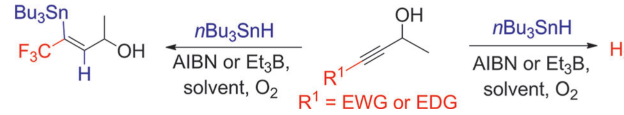


Skeleton in the closet: The title reaction enables the development of the first catalytic β,γ-selective Diels–Alder [4+2] annulation of α,β-unsaturated γ-butyrolactams (see scheme; Boc = *tert*-butoxycarbonyl, Ts = 4-toluenesulfonyl). This process provides a direct method for the enantioselective construction of bi- or tricyclic dihydropyranopyrrolidin-2-one skeletons in only one step.

Synthetic Methods

M. S. Oderinde, R. D. J. Froese, M. G. Organ* ———— **11334–11338**

2,2′-Azobis(2-methylpropionitrile)-Mediated Alkyne Hydrostannylation: Reaction Mechanism



Not as radical as you think: The free-radical hydrostannylation of alkynes has been extensively studied and while every published mechanism involves solely radical intermediates, this appears not to be correct. Trace molecular oxygen is necessary for any radical-mediated hydrostannylation to occur with a wide selection of alkynes, thus leading to a proposed hybrid single-electron transfer/radical propagation mechanism. AIBN = 2,2′-azobis(2-methylpropionitrile).

Sialic Acids

C. Navuluri, D. Crich* ——— 11339 – 11342

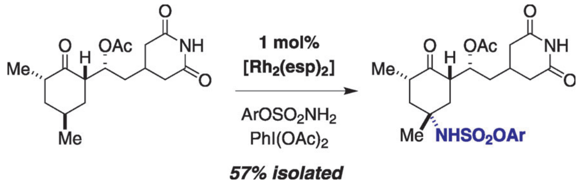
Chemical Diversification of Sialic Acid Glycosides by Stereospecific, Chemoselective Deamination

Late bloomer: Nitrosation of peracetylated sialic acid glycosides followed by treatment with sodium trifluoroethoxide and then a suitable nucleophile enables the late-stage modification of these glycosides with stereospecific replacement of the acetamido group. This method should enable access to many glycoside derivatives with a minimum of synthetic effort.

C–H Functionalization

J. L. Roizen, D. N. Zalatan,
J. Du Bois* ——— 11343 – 11346

Selective Intermolecular Amination of C–H Bonds at Tertiary Carbon Centers

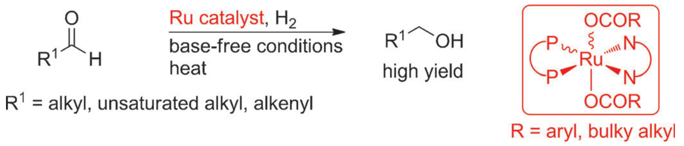


C–H insertion: A method for intermolecular amination of tertiary C–H bonds is described that uses limiting amounts of substrate and a convenient phenol-derived nitrogen source. Structure-selectivity and mechanistic studies suggest that steric interaction between the substrate and active oxidant is the principal determinant of product selectivity.

Catalytic Hydrogenation

P. Dupau,* L. Bonomo,
L. Kermorvan ——— 11347 – 11350

Unexpected Role of Anionic Ligands in the Ruthenium-Catalyzed Base-Free Selective Hydrogenation of Aldehydes

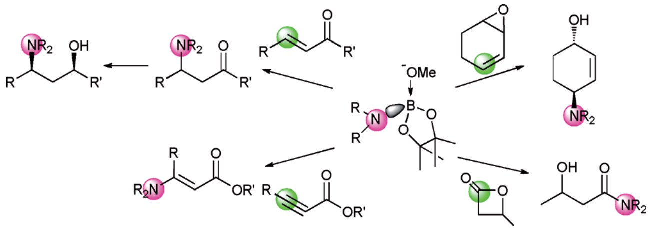


Bigger and better: The replacement of anionic chloride ligands in Noyori-type [(diamine)(diphosphine)$\mathrm{RuCl_2}$] catalysts with bulky carboxylate ligands enabled the efficient selective hydrogenation of a variety of aldehydes under base-free conditions (see scheme). Turnover numbers of up to 100 000 were reached in the presence of a bulky carboxylic acid co-catalyst. This type of catalytic system probably operates through an inner-sphere mechanism.

Organocatalysis

C. Solé, E. Fernández* ——— 11351 – 11355

Alkoxide Activation of Aminoboranes towards Selective Amination



Piece of the (inter)action: The interaction of alkoxides with the sp^2 Bpin (pin = pinacol) moiety in aminoboranes forms the in situ Lewis acid–base adduct $[\mathrm{RO}^- \rightarrow \mathrm{B(OR)_2}-\mathrm{N(R')_2}]$ which enables the amino moiety to react as a strong nucleophile with several electrophiles, thus providing amino alcohols, β-enamino esters, and β-hydroxy amides in a direct and remarkably selective way (see scheme).

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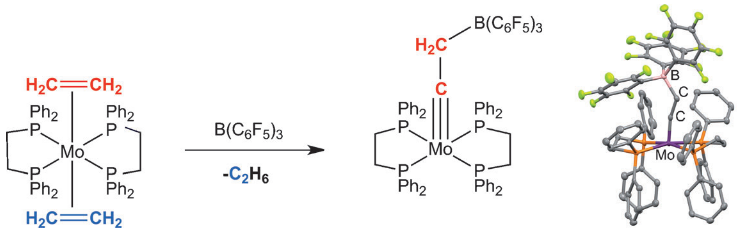
Multiple Bonds

T. E. Stennett, M. F. Haddow,
D. F. Wass* ____________ 11356 – 11359

Alkene to Carbyne: Tandem Lewis Acid Activation and Dehydrogenation of a Molybdenum Ethylene Complex



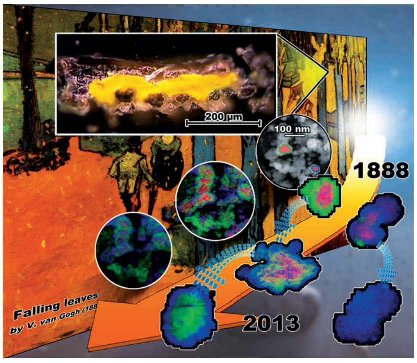
Carbyne formation: Treatment of a molybdenum ethylene complex with $B(C_6F_5)_3$ induces ditopic activation of an ethylene ligand and acceptor-assisted ethane elimination to generate a novel type of zwitterionic carbyne complex (see scheme).

Paint Degradation

H. Tan, H. Tian,* J. Verbeeck, L. Monico, K. Janssens,
G. Van Tendeloo ________ 11360 – 11363

Nanoscale Investigation of the Degradation Mechanism of a Historical Chrome Yellow Paint by Quantitative Electron Energy Loss spectroscopy Mapping of Chromium Species

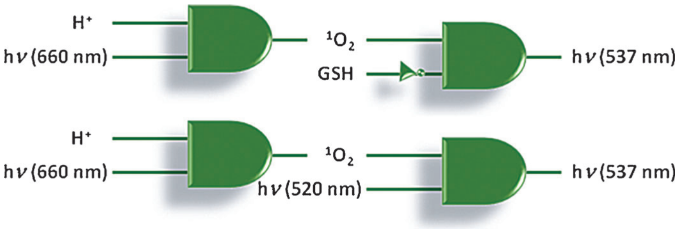
Getting the picture: The investigation of 100 year old chrome yellow paint by transmission electron microscopy and spectroscopy has led to the identification of four types of core–shell particles. This nanoscale investigation has allowed a mechanism to be proposed for the darkening of some bright yellow colors in Van Gogh's paintings (e.g. in *Falling leaves* (*Les Alyscamps*), 1888).



Chemical Logic Gates

S. Erbas-Cakmak,
E. U. Akkaya* ____________ 11364 – 11368

Cascading of Molecular Logic Gates for Advanced Functions: A Self-Reporting, Activatable Photosensitizer

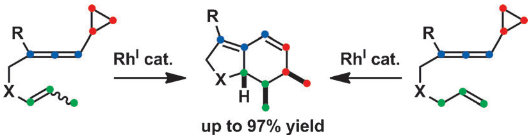


Logical progress: Independent molecular logic gates have been designed and characterized. Then, the individual molecular logic gates were coerced to work together within a micelle. Information relay between the two logic gates was achieved through the intermediacy of singlet oxygen. Working together, these concatenated logic gates result in a self-reporting and activatable photosensitizer. GSH = glutathione.

Cyclization Reactions

K. Sugikubo, F. Omachi, Y. Miyanaga, F. Inagaki, C. Matsumoto,
C. Mukai* ____________ 11369 – 11372

Rhodium(I)-Catalyzed Cycloisomerization of Alkene-Substituted Allenylcyclopropanes: Stereoselective Formation of Bicyclo[4.3.0]nonadienes



A productive channel for pent-up energy: The $[\{RhCl(CO)_2\}_2]$-catalyzed ring-opening of both *E* and *Z* 1-cyclopropylocta-1,2,6-trienes exclusively produced *cis*-4,5-dimethylbicyclo[4.3.0]nona-1(9),2-dienes with three contiguous stereogenic centers. When this transformation was applied to the 1,2,7-triene double-bond isomers, the same products were formed in a completely stereoselective manner (see scheme).

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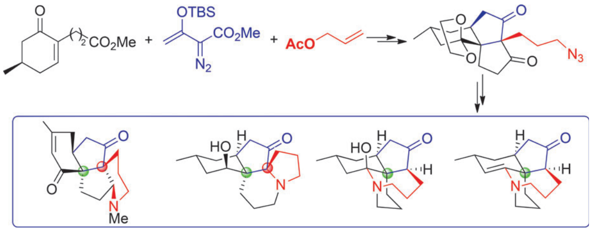
Natural Product Synthesis

S.-H. Hou, Y.-Q. Tu,* L. Liu, F.-M. Zhang,
S.-H. Wang,*
X.-M. Zhang ______ **11373 – 11376**

Divergent and Efficient Syntheses of the *Lycopodium* Alkaloids
(−)-Lycojaponicumin C, (−)-8-Deoxyserratinine, (+)-Fawcettimine, and (+)-Fawcettidine

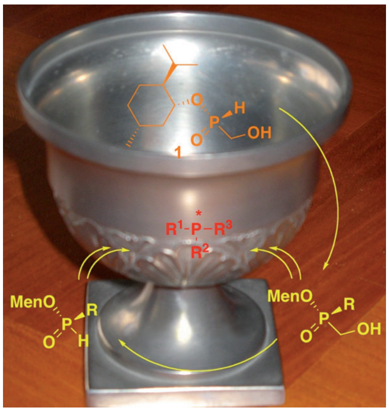


Four from one: The four title alkaloids (structures shown in blue box) have been synthesized by using a common versatile intermediate with a 6/5/5 tricyclic skeleton. This tricyclic intermediate could be easily assembled by using an intramolecular carbene addition/cyclization and a Dieckmann condensation/Tsuji–Trost allylation as key steps.

Asymmetric Synthesis

O. Berger,
J.-L. Montchamp* ______ **11377 – 11380**

A General Strategy for the Synthesis of P-Stereogenic Compounds

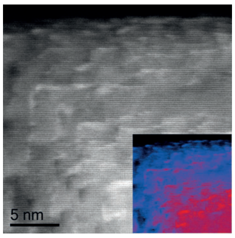


A great leap forward toward the general synthesis of P-stereogenic compounds: Heating H_3PO_2 with (−)-menthol and paraformaldehyde gives easily crystallized menthyl hydroxymethyl-*H*-phosphinate (**1**). From this product, virtually any P-stereogenic compound can be synthesized (see picture).

C–H activation

P. Schwach, M. Willinger, A. Trunschke,*
R. Schlögl ______ **11381 – 11384**

Methane Coupling over Magnesium Oxide: How Doping Can Work



Electronic doping of magnesium oxide catalysts has an effect on the oxidative coupling of methane. Highly active sites can be created by co-modification of MgO with iron and gold in ppm quantities.

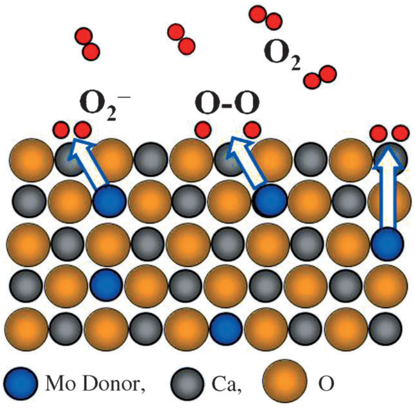
Oxygen Activation

Y. Cui, X. Shao, M. Baldofski, J. Sauer,
N. Nilius,* H.-J. Freund ______ **11385 – 11387**

Adsorption, Activation, and Dissociation of Oxygen on Doped Oxides

Back Cover

Charge transfer in the presence of dopants is relevant for the adorption and activation of small molecules, such as O_2. Scanning tunneling microscopy and DFT calculations provide evidence for the formation of strongly bound superoxo species on chemically inert, Mo-doped CaO films (see picture). This oxygen surface species shows a high propensity to dissociate. Dopants could also be important for the activation of hydrocarbons on inert oxides.



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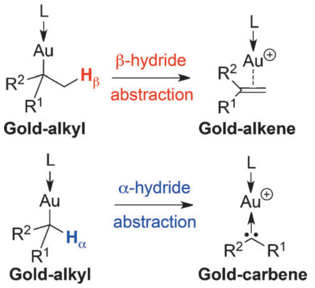
Gold Complexes

G. Ung, G. Bertrand* ____ 11388 – 11391

β- and α-Hydride Abstraction in Gold(I) Alkyl Complexes



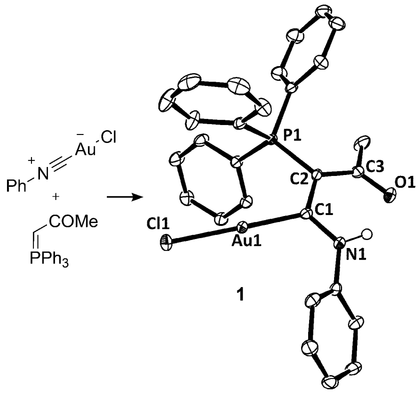
Why not both? Both β- and α-hydrogen atoms of gold alkyl complexes are hydridic enough to be abstracted, opening a new route to gold–alkene and gold–carbene complexes, respectively.

Carbenes

E. González-Fernández, J. Rust, M. Alcarazo* ____ 11392 – 11395

Synthesis and Reactivity of Metal Complexes with Acyclic (Amino)(Ylide)Carbene Ligands

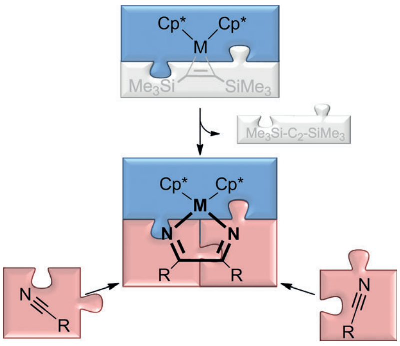
No cycle required: The straightforward synthesis of acyclic (amino)(ylide)carbene gold complexes was achieved by reaction of isocyanide gold complexes with phosphorus and arsenic ylides as well as electron-rich olefins. Their ability to form bimetallic species and to act as ligand-transfer reagents has also been established.



C–C Coupling

L. Becker, P. Arndt, H. Jiao, A. Spannenberg, U. Rosenthal* ____ 11396 – 11400

Nitrile–Nitrile C–C Coupling at Group 4 Metallocenes to Form 1-Metalla-2,5-diazacyclopenta-2,4-dienes: Synthesis and Reactivity



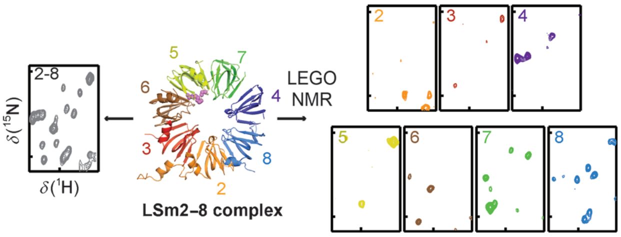
The C–C coupling of aryl nitriles at Group 4 metallocenes leads to unusual ring-strained 1-metalla-2,5-diaza-cyclopenta-2,4-dienes. The structural, energetic, and chemical properties of these complexes are described. The reactions of these compounds towards CH_3CN, H_2, CO_2, and HCl usually lead to the release of one nitrile and its replacement by different co-substrates.

Protein NMR Spectroscopy

M. Mund, J. H. Overbeck, J. Ullmann, R. Sprangers* ____ 11401 – 11405

LEGO-NMR Spectroscopy: A Method to Visualize Individual Subunits in Large Heteromeric Complexes

Front Cover



Seeing the big picture: Asymmetric macromolecular complexes that are NMR active in only a subset of their subunits can be prepared, thus decreasing NMR spectral complexity. For the hetero heptameric LSm1–7 and LSm2–8 rings NMR spectra of the individual subunits of the complete complex are obtained, showing a conserved RNA binding site. This LEGO-NMR technique makes large asymmetric complexes accessible to detailed NMR spectroscopic studies.

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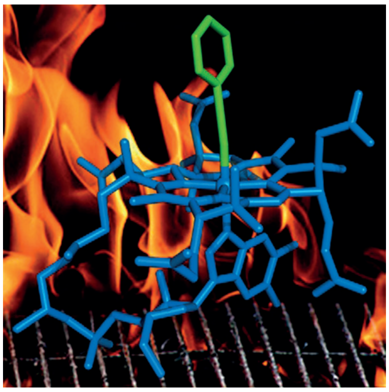
Organometallic B_{12} Chemistry

M. Ruetz, R. Salchner, K. Wurst,
S. Fedosov, B. Kräutler* **11406 – 11409**

Phenylethynylcobalamin: A Light-Stable and Thermolysis-Resistant Organometallic Vitamin B_{12} Derivative Prepared by Radical Synthesis

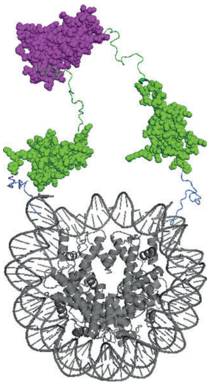


Don't take this antivitamin! 2-Phenylethynylcobalamin (see picture) was prepared in a newly developed radical reaction using cob(II)alamin and 1-iodo-2-phenylethyne. It has an exceptionally short organometallic bond and is a remarkably light-stable and heat-resistant organometallic cobalamin. It is bound well by two important proteins of the human B_{12} transport system and has properties that are as expected for a new type of an "antivitamin B_{12}".

NMR Spectroscopy

N. Rezaei-Ghaleh,* F. Klama, F. Munari,
M. Zweckstetter* **11410 – 11414**

Predicting the Rotational Tumbling of Dynamic Multidomain Proteins and Supramolecular Complexes

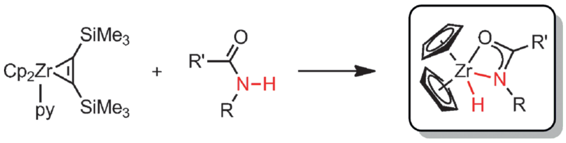


Time is of the essence: The rotational motion of biomolecules depends on intra- and intermolecular interactions and thus on distinct functional states. A new method, called HYCUD accurately predicts rotational correlation times in complex dynamic systems. It gives insights into the motional behavior of multidomain proteins in their free form and in supramolecular complexes.

Zirconocene Hydrido Complexes

M. Haehnel, J. C.-H. Yim, L. L. Schafer,*
U. Rosenthal* **11415 – 11419**

Facile Access to Tuneable Schwartz's Reagents: Oxidative Addition Products from the Reaction of Amide N–H Bonds with Reduced Zirconocene Complexes

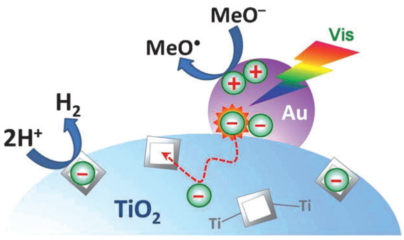


On the tracks of Schwartz's reagent: Two zirconocene hydrido amidate complexes are synthesized by formal oxidative addition of amide N–H bonds to reduced zirconocene fragments. Insertion reactions with alkenes show a different behavior than Schwartz's reagent by forming branched insertion products. The insertion product and the hydrido complex are characterized by X-ray analysis.

Water Reduction

J. B. Priebe, M. Karnahl, H. Junge,
M. Beller, D. Hollmann,
A. Brückner* **11420 – 11424**

Water Reduction with Visible Light: Synergy between Optical Transitions and Electron Transfer in Au-TiO_2 Catalysts Visualized by In situ EPR Spectroscopy



Golden electrons: Visible light excites conduction electron transfer from gold particles to support vacancies where they are taken up by protons to produce hydrogen. This transfer process was visualized by in situ EPR spectroscopy.

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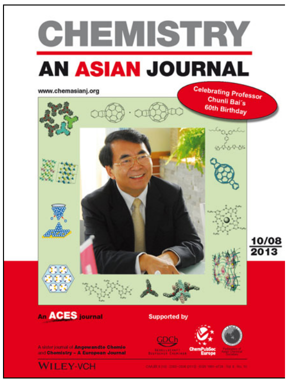

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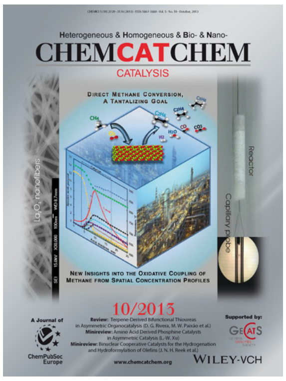

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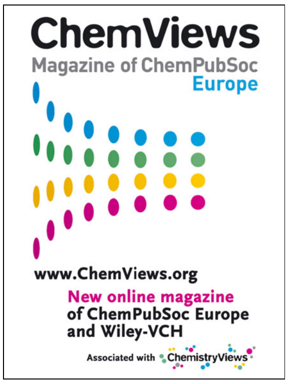

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In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and it should not mention graphical elements, tables, or references within the paper.

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