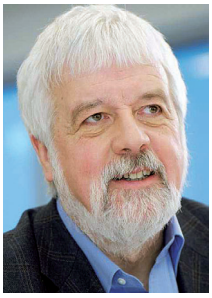
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

Editorial



Author Profile

"I like refereeing because it gives me a more original picture of the paper.
The greatest scientific advance in the next decade will be the transition to sustainable and biobased chemistry …"
This and more about Jürgen O. Metzger can be found on page 9237.

News


C. Amatore


B. L. Feringa


P. Gölitz


G. J. Hutchings


J. A. Lercher


M. Orrit


M. Verdaguer

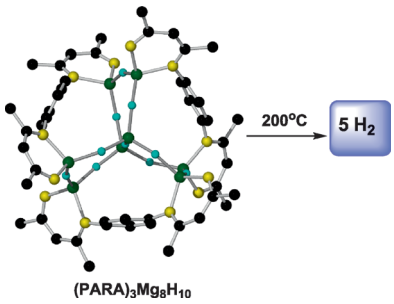

B. M. Weckhuysen

Contents

Books

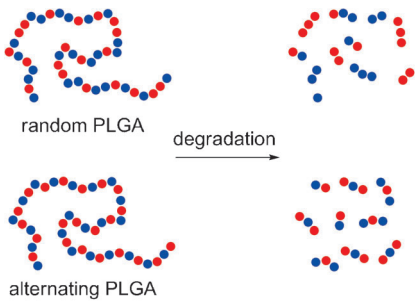
Highlights

Hydrogen Storage



Hydride carrier: Making significant progress on the road towards practical hydrogen storage materials for mobile applications, inorganic chemistry shows us how to build the largest ligand-supported magnesium hydride cluster known to date (see picture).

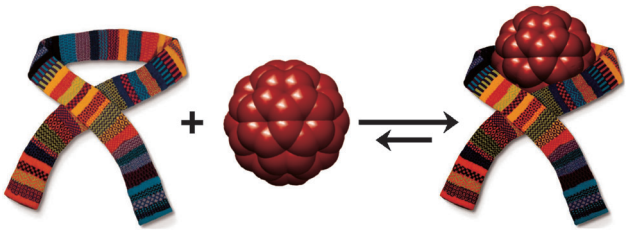
Polymer Sequences



It's all in the sequence: The primary structure of poly(lactic-*co*-glycolic acid) (PLGA), a member of the most widely used class of biodegradable polymers employed in biomedical applications, is demonstrated to strongly influence its degradation properties. Experimental studies evidenced the beneficial effect of ordered monomer sequences on the material properties (see picture).

Minireviews

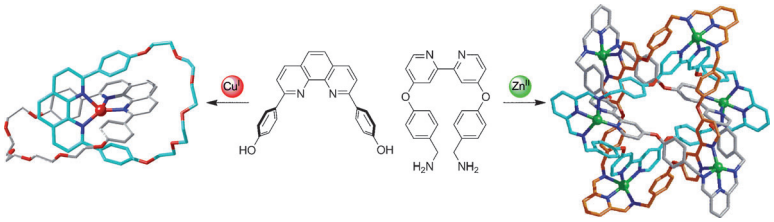
Fullerene Receptors



All wrapped up: In the field of fullerene recognition, chemists are currently facing new challenges dealing with the selective extraction of higher fullerenes, their chiral resolution, or their organization in molecular materials. In this regard, the new generation of macrocyclic hosts looks particularly promising and has already allowed important breakthroughs.

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*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (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.

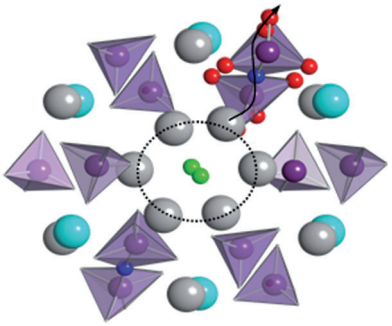
Reviews



Knots and crossings: Metal ions have been employed in diverse ways in the assembly of mechanically interlocked architectures (see scheme). The range of product topologies spans from catenanes and rotaxanes to trefoil knots, Solomon links, and Borromean rings.

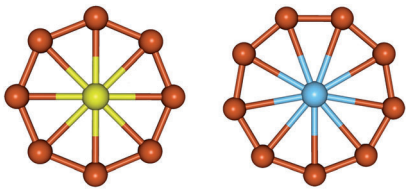
Interlocked Molecules

Communications



Germanium-based apatite compounds are fast oxide-ion conductors for potential use in fuel cells. A combination of solid-state ^{17}O NMR spectroscopy, atomistic modeling, and DFT techniques help to elucidate oxygen defect sites and novel cooperative mechanisms of ion conduction. The picture shows oxygen diffusion in the studied apatite compound from molecular dynamics simulations.

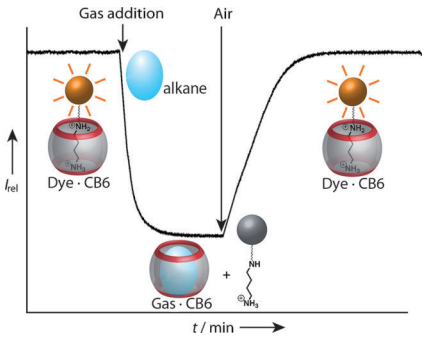
Fuel Cells



Perfect symmetry: Photoelectron spectroscopy and theoretical calculations show that the B_8 and B_9 rings are stabilized by the metal atoms in $Co©B_8^-$ and $Ru©B_9^-$, which possess D_{8h} and D_{9h} symmetry, respectively (see picture). The bonding between the metal atom and the boron ring is described by six delocalized σ electrons and six delocalized π electrons, which result in double aromaticity.

Aromaticity

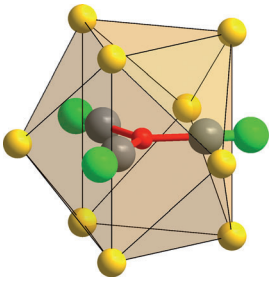
Hydrocarbons are no longer afraid of water when they are reversibly encapsulated by cucurbituril (see picture). The pumpkin-shaped molecular container displays a high affinity and selectivity towards neutral molecules in salt-free aqueous solutions. A supramolecular sensing ensemble, composed of cucurbit[6]uril and an anchored indicator dye, is introduced as a highly sensitive fluorescence-based online detection tool for gas binding in solution.



Supramolecular Chemistry

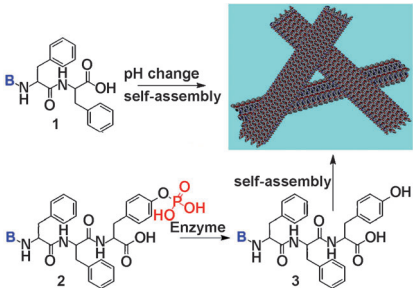
Contents

More than meets the eye: The trigonal-planar complex $[Co(CN)_3]^{6-}$ (see structure, Co red, C gray, N green; alkaline-earth-metal counterions are yellow) has some surprises in store. The CN ligand displays variation in bond length and charge, and Co follows a closed-shell (d^{10}) concept.

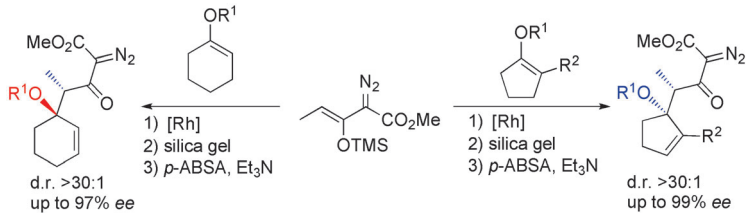


Metalates

Watson–Crick interactions: The conjugation of nucleobases (B = thymine, adenine, cytosine, and guanine; see picture) with small peptides affords a novel kind of supramolecular nanofibers and hydrogelators, which exhibit a high biocompatibility and biostability and are regarded as promising new biomaterials.

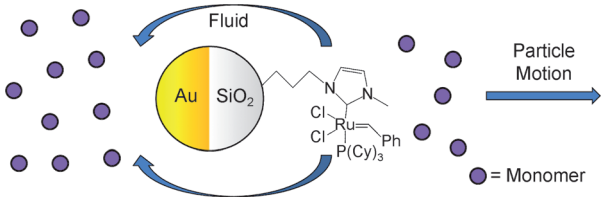


Supramolecular Hydrogels



Diastereoselectivity in control: The synthetic utility of the C–H functionalization/Cope rearrangement reaction has been greatly expanded by the design of substrates that will react through a boat transition state instead of a chair transition state. The products are formed with the opposite diastereoselectivity as previously obtained (see scheme, ABSA = acetamidobenzenesulfonylazide).

C–H Functionalization

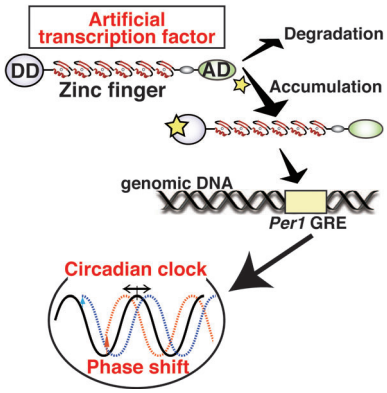


Polymer powered! A polymerization reaction has been used to power the first micromotor outside biological systems. The motor employs a form of Grubbs' catalyst asymmetrically bound to gold–silica Janus microspheres (see picture). These motors show increased diffusion of up to 70% when placed in solutions of the monomer. The motors also exhibit chemotaxis when placed in a monomer gradient.

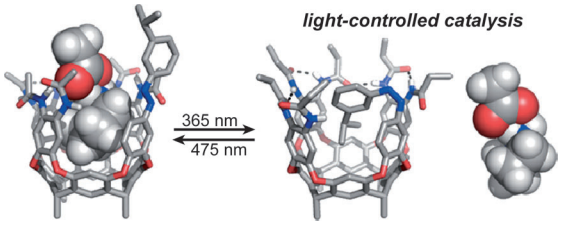
Micromotors

Contents

I got rhythm: The circadian clock is driven by transcription–translation feedback loops. The circadian time can be altered by creating an artificial zinc finger protein specifically binding to the glucocorticoid responsive element (GRE) on the *Period1* promoter (see picture; DD = destabilizing domain, AD = activation domain). This artificial protein directly controls the clock machinery.

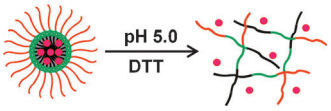


Circadian Rhythm



Catalytic guest stars: A cavitand with an azobenzene wall adopts an introverted shape when irradiated with UV light. This conformation has been characterized in solution and the solid state and is used to control guest binding. By incorporating an organocatalyst guest, the rate of the Knoevenagel condensation is controlled with light.

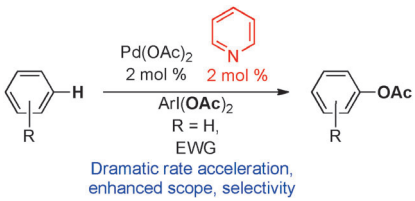
Supramolecular Catalysis



On the double: A highly packed interlayer-crosslinked micelle (HP-ICM) with pH and reduction sensitivity was developed for targeted drug release (see picture; DTT = dithiothreitol, red circles = doxorubicin). The HP-ICM suppresses drug leakage in blood circulation while rapidly releasing drug inside lysosomes of cancer cells. Biological studies revealed the potential of the dual-sensitive HP-ICM in cancer treatment.

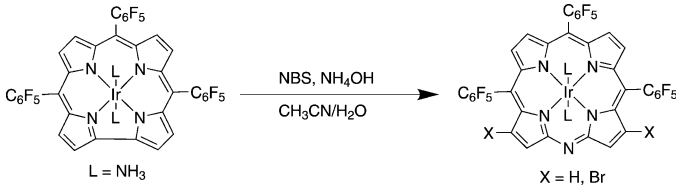
Drug Delivery

Less is more: The rational optimization and general applicability of the catalytic system $Pd(OAc)_2$/pyridine is described (see scheme). The catalyst shows excellent reactivity in the C–H oxygenation of simple aromatic substrates. The Pd/pyridine ratio is critical as the use of one equivalent of pyridine per Pd center leads to dramatic enhancements in both reactivity and site selectivity in comparison to $Pd(OAc)_2$ alone.



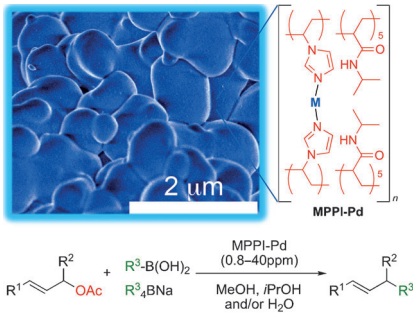
C–H Activation

Contents



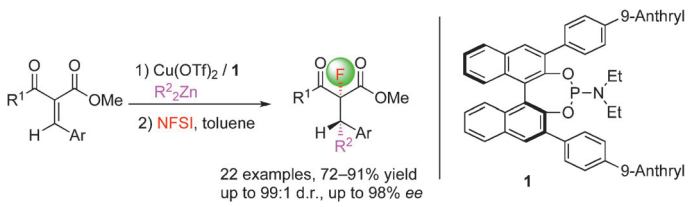
Corrole Expansion

A new route to rare porphyrinoids: The non-innocence of the corrole ring allows the oxidative ring insertion of a nitrogen atom under mild conditions (see scheme; NBS = *N*-bromosuccinimide). The resulting *meso*-substituted azaporphyrins exhibit high-energy Soret absorption bands and red luminescence. This new synthetic route will allow for the development of novel azaporphyrin complexes with relevance to the study of biomimetic oxidations.



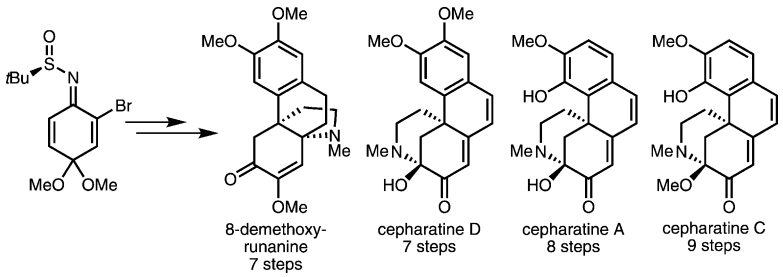
Supramolecular Catalysts

Gobs of globules: A polymeric imidazole/acrylamide palladium catalyst, MPPI-Pd (M = $Pd^{II}Cl$ and Pd^{0}), was utilized for the allylic arylation/alkenylation of allylic esters with aryl/alkenylboronic acids and tetraaryl borates. Low catalyst loadings efficiently promoted the reaction with a catalytic turnover number of 20000–1250000. The catalyst can be reused without loss of catalytic activity.



Asymmetric Catalysis

Long arm of the law: The long-armed phosphoramidite **1** was used as a catalyst for the title reaction of acyclic alkylidene β-ketoesters with dialkylzinc and fluorinating reagents. The products, containing adjacent carbon- and fluorine-substituted stereocenters, are obtained in high yield as well as diastereo- and enantioselectivity. NSFI = *N*-fluorobenzenesulfonimide.

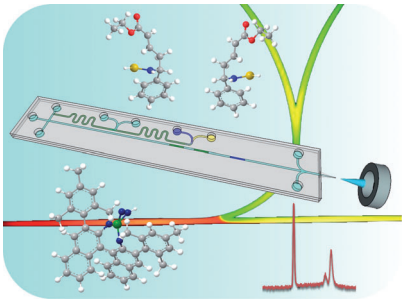


Natural Product Synthesis

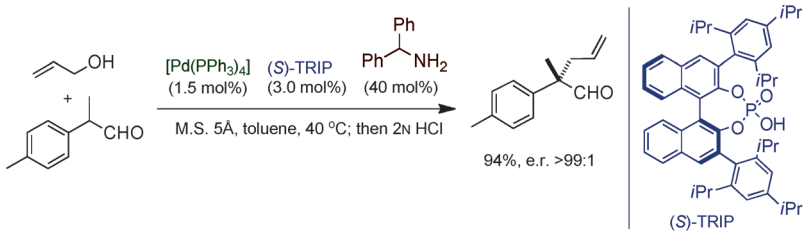
All together! A unified synthetic strategy has resulted in the first enantioselective total syntheses of the natural products 8-demethoxyrunanine and cepharatines A, C, and D.

Contents

Organocatalysis meets chip MS: By integrating asymmetric organocatalysis and analysis on a chip (see picture), optimization of reactions can be achieved with minimal consumption of resources in a short period of time.

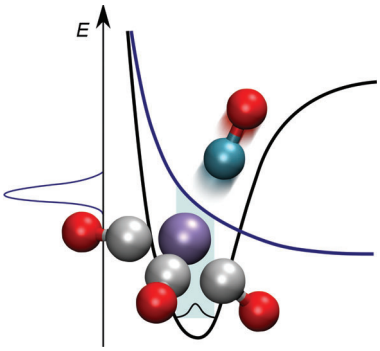


Lab on a Chip



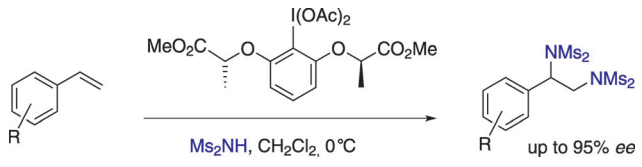
Triple catalysis: The title reaction between α-branched aldehydes and allylic alcohols, which generates all-carbon quaternary stereogenic centers, constitutes the first asymmetric Tsuji–Trost-type α-allylation of carbonyl compounds with allylic alcohol (see scheme). This reaction is catalyzed by three different species, $[Pd(PPh_3)_4]$, the chiral Brønsted acid TRIP, and benzhydryl amine.

Triple Catalysis



Put a number on it: Absolute cross-sections for dissociative electron attachment (DEA) to the common precursor molecule cobalt tricarbonyl nitrosyl in the gas phase are reported (see scheme, Co dark blue, O red, C gray, N light blue) along with the branching ratios for the negative ions and the electron affinities for the neutral radical fragments. Further, a general mechanism of DEA is proposed for metal–carbonyl compounds.

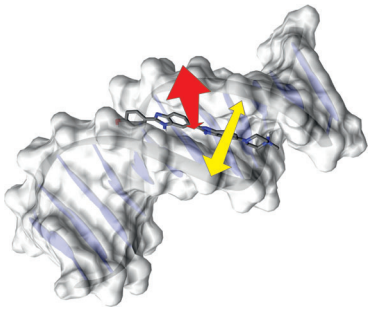
Gas-Phase Chemistry



Metal-free and asymmetric: The first enantioselective diamination of styrenes simply requires a chiral hypervalent iodine(III) reagent as an oxidant and bismesylimide as a nitrogen source (see scheme, Ms = methanesulfonyl). The reaction proceeds under mild conditions and with high enantiomeric excess.

Asymmetric Synthesis

Contents



Riding the waves: In a DNA–ligand complex, the time-dependent Stokes shift shows initial oscillation. Molecular dynamics simulations help assign this ripple to coherent in/out motion of the ligand together with breathing of the minor groove (see picture).

Femtosecond Spectroscopy

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

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

This article is available online free of charge (Open Access)

Service

Contents

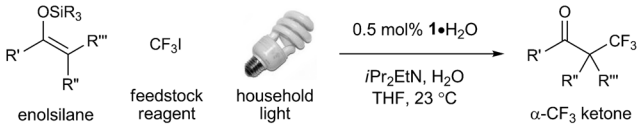
Corrigendum

Angew. Chem. Int. Ed. **2011**, *50*

DOI 10.1002/anie.201101861

This Communication contains a typesetting mistake. In Table 2, inadvertently the same chemical equation was used as in Table 3. The correct Table 2 is shown below.

Table 2: Trifluoromethylation of enolsilanes: ketone scope.



Entry	Product	Yield[a]
R =	*1*: H 92%	*4*: I 83%
	2: OMe 78%	*5*: Br 85%
	3: CN 66%	*6*: Cl 85%
		7: F 80%
8: 72%[b]		
9: 74%[c,d]		
10: X = O[e] 64%		*12*: R = Boc[e] 73%
11: X = S[e] 72%		*13*: R = Cbz[e] 59%
14: 68%[e]	*15*: 84%[b]	*16*: 76%

[a] Yield of isolated product; SiR_3 = TIPS unless otherwise noted. [b] TES ether employed. [c] TBS ether employed. [d] 2.2:1 d.r. [e] With $NaHCO_3$ in MeCN and TES ether.