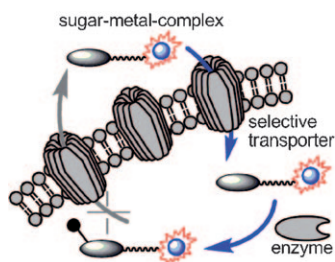


CONCEPTS

Bioinorganic Chemistry

M. Gottschaldt,*
U. S. Schubert 1548–1557

Prospects of Metal Complexes Peripherally Substituted with Sugars in Biomedical Applications



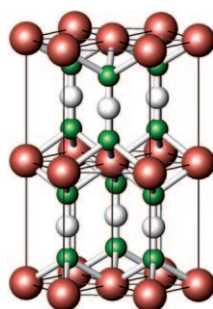
Sugar is good for you! The latest developments in the field of sugar substitution of metal complexes and its influence on the action of these complexes in biological systems are discussed (see figure). In particular, the progress in applications as selective tracers and therapeutics in connection to the underlying chemical structure is highlighted.

COMMUNICATIONS

Iron Carbodiimide

X. Liu, L. Stork, M. Speldrich,
H. Lueken,
R. Dronskowski* 1558–1561

FeNCN and Fe(NCNH)₂: Synthesis, Structure, and Magnetic Properties of a Nitrogen-Based Pseudo-oxide and -hydroxide of Divalent Iron

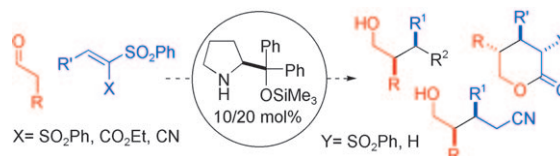


Iron man challenge: Iron carbodiimide, FeNCN, and its precursor iron (bis)-monohydrocyanamide, Fe(NCNH)₂, have been synthesized and physically characterized. Both FeNCN and Fe(NCNH)₂ exhibit nitrogen-mediated antiferromagnetic superexchange interactions with reduced magnetic moments very similar, but not identical, to the correlated 3d oxides.

Organocatalysis

A. Landa, M. Maestro, C. Masdeu,
Á. Puente, S. Vera, M. Oiarbide,
C. Palomo* 1562–1565

Highly Enantioselective Conjugate Additions of Aldehydes to Vinyl Sulfones



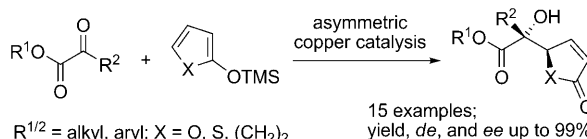
Joined together, organocatalysts aldehydes and sulfones: A diaryl prolinol silyl ether was found to catalyze efficiently and enantioselectively the con-

jugate addition of aldehydes to vinyl sulfones (see scheme). The ample synthetic utility of the resulting adducts is illustrated.

Asymmetric Catalysis

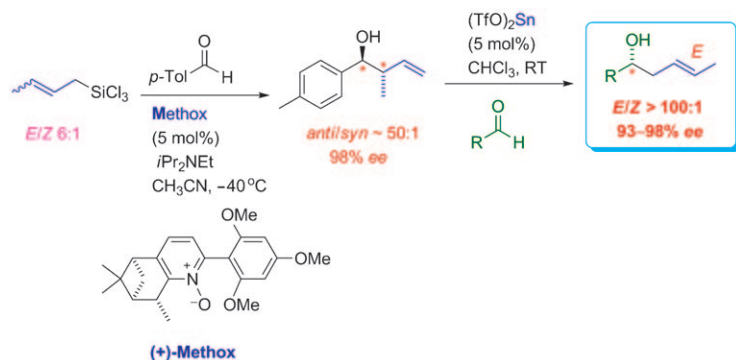
M. Frings, I. Atodiresei, J. Runsink,
G. Raabe, C. Bolm* 1566–1569

Catalyzed Vinylogous Mukaiyama Aldol Reactions with Controlled Enantio- and Diastereoselectivities



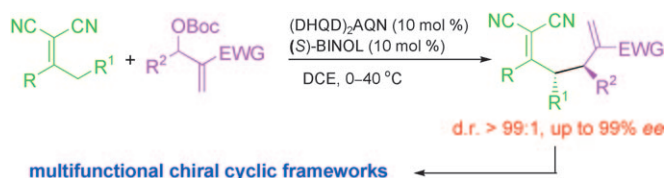
In control: A new catalytic vinylogous Mukaiyama aldol reaction provides products with high diastereo- and enantioselectivities (up to 99% *de* and *ee*; see scheme). The relative and abso-

lute stereochemistry of a representative product was rigorously assigned by NMR and CD spectroscopies (measured and calculated), X-ray diffraction, and quantum-chemical calculations.



Kinetic refinery: A practical, highly stereoselective, two-step catalytic protocol for the α -allylation of aldehydes, starting from crotyltrichlorosilanes, has been developed (see scheme). In each reaction step, one of the stereoisomers reacted faster than the other, which

resulted in a kinetic stereochemical (*E/Z*) self-refinement of the system and led to the formation of virtually enantiomerically and geometrically pure linear homoallylic alcohols in high yield.



The first highly enantioselective allylic-allylic alkylation of α,α -dicycycloalkenes and Morita-Baylis-Hillman carbonates by dual catalysis of (DHQD)₂AQN and (*S*)-BINOL has been investigated. Excellent stereoselectivities have been achieved for a broad spectrum of substrates (d.r.

> 99:1, up to 99% *ee*). The multifunctional allylic products could be efficiently converted to a range of complex chiral cyclic frameworks. EWG = electron-withdrawing group, (DHQD)₂AQN = hydroquinidine (anthraquinone-1,4-diyl) diether, (*S*)-BINOL = (*S*)-(-)-1,1'-bi-2-naphthol.

Enantioselective Allylation

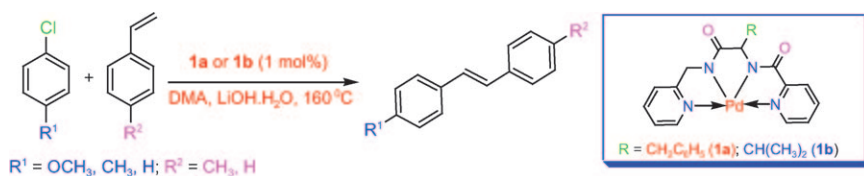
A. V. Malkov,* M. A. Kabeshov, M. Barlog, P. Kočovský* ... 1570–1573

Enantioselective and Catalytic Method for α -Crotylation of Aldehydes with a Kinetic Self-Refinement of Stereochemistry

Organocatalysis

H.-L. Cui, J. Peng, X. Feng, W. Du, K. Jiang, Y.-C. Chen* ... 1574–1577

Dual Organocatalysis: Asymmetric Allylic-Allylic Alkylation of α,α -Dicycycloalkenes and Morita-Baylis-Hillman Carbonates



Structurally well defined and thermally stable Pd^{II} complexes, derived from N4-tetradentate dicarboxyamido/dipyridyl ligands, were evaluated as catalysts for the Heck reactions of deactivated aryl chlorides and olefins (see

scheme). The concept of using an anionic carboxyamido as an ancillary ligand for palladium demonstrated here provides a new opportunity for the development of phosphine-free transition-metal catalysis.


C–C Coupling

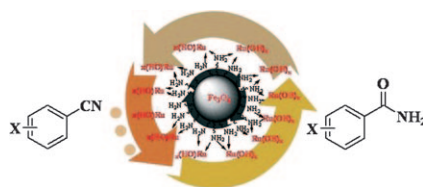
P. Srinivas, P. R. Likhar, D. H. Maheswaran, B. Sridhar, K. Ravikumar, M. L. Kantam* ... 1578–1581

N4-Tetradentate Dicarboxyamido/Dipyridyl Palladium Complexes as Robust Catalysts for the Heck Reaction of Deactivated Aryl Chlorides

Nanocatalysts

V. Polshettiwar,
R. S. Varma* 1582–1586

 **Nanoparticle-Supported and Magnetically Recoverable Ruthenium Hydroxide Catalyst: Efficient Hydration of Nitriles to Amides in Aqueous Medium**




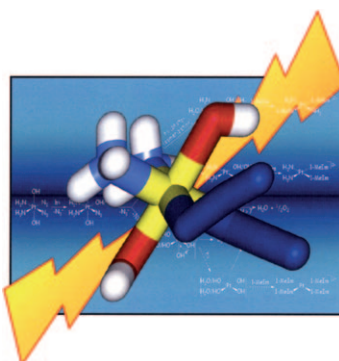
Magnetic attraction not filtration: A magnetic nanoparticle-supported ruthenium hydroxide catalyst (see figure) was readily prepared from inexpensive starting materials and shown to catalyze the hydration of nitriles with excellent yield in a benign aqueous medium. Catalyst recovery using an external magnetic field, superior activity, and the inherent stability of the catalyst system are additional sustainable attributes of this protocol.

FULL PAPERS

Bioinorganic Chemistry

H. I. A. Phillips, L. Ronconi,
P. J. Sadler* 1588–1596


 **Photoinduced Reactions of *cis,trans,cis*-[Pt^{IV}(N₃)₂(OH)₂(NH₃)₂] with 1-Methylimidazole**

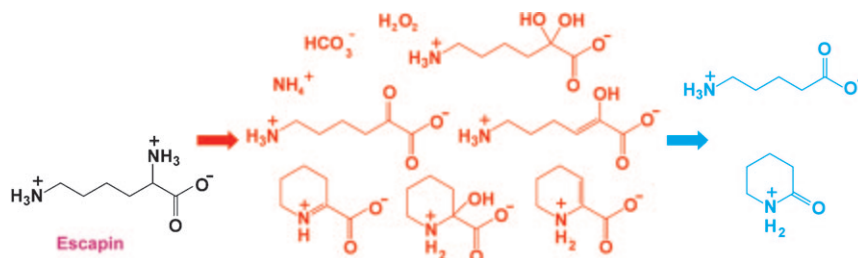


Lighting up new platinum anticancer complexes: Photoactivation of a platinum(IV) diazido anticancer complex in the presence of a derivative of imidazole, an important constituent of biomolecules, gives surprising photo-products, including a tetrakis imidazole platinum(II) adduct (see figure), together with free azide, dioxygen and ammonia.

Natural Products

M. Kamio, K.-C. Ko, S. Zheng,
B. Wang, S. L. Collins, G. Gadda,
P. C. Tai, C. D. Derby* 1597–1603

 **The Chemistry of Escapin: Identification and Quantification of the Components in the Complex Mixture Generated by an L-Amino Acid Oxidase in the Defensive Secretion of the Sea Snail *Aplysia californica***




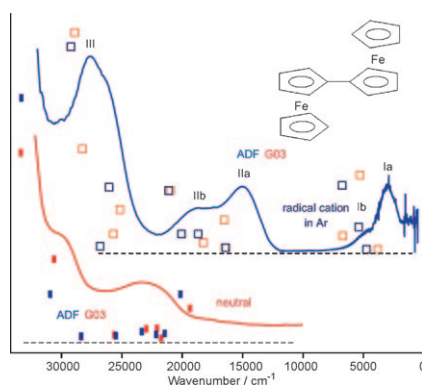
A complex mixture of products in an enzymatic reaction: *Aplysia californica* releases amino acid oxidase and its

substrate lysine in defensive secretions to produce a mixture of multiple compounds (see figure).

Mixed-Valent Compounds

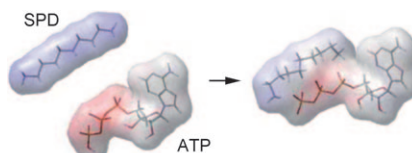
R. Warratz, H. Aboulfadl, T. Bally,*
F. Tuczek* 1604–1617

 **Electronic Structure and Absorption Spectra of Biferrocenyl and Bisfulvalenide Diiron Radical Cations: Detection and Assignment of New Low-Energy Transitions**



New transitions: Low-energy electronic transitions have been detected spectroscopically in the Fe^{II}–Fe^{III} mixed-valent biferrocenyl radical cation, but are absent in the spectra of the neutral analogue. They have been assigned by time-dependent DFT calculations (squares in figure). Analogous investigations were performed for the bisfulvalenide Fe^{II}–Fe^{III} radical cation.

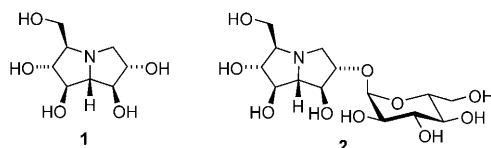
A complex rotation: The solution conformation of spermidine (SPD) was elucidated by using diastereospecifically deuterated and ^{13}C -labeled derivatives to diagnose the orientation of seven conformationally relevant bonds. NMR coupling constants were determined for a complex formed from spermidine and adenosine triphosphate (ATP; see figure).



Conformation Analysis

*K. Maruyoshi, K. Nonaka, T. Sagane, T. Demura, T. Yamaguchi, N. Matsumori, T. Oishi, M. Murata** 1618–1626

Conformational Change of Spermidine upon Interaction with Adenosine Triphosphate in Aqueous Solution



Selective glucosylation: Total synthesis of naturally occurring casuarine (**1**) and the first total synthesis of casuarine 6-*O*- α -glucoside (**2**) were achieved through complete stereoselective nitron cycloaddition, Tamao–Fleming oxidation and selective α -glucosylation

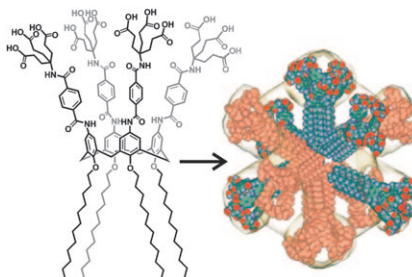
as key steps. Biological assays of the two compounds proved their strong and selective inhibitory properties towards glucoamylase NtMGAM and trehalase Tre37A, respectively, which place them among the most powerful inhibitors of these enzymes.

Natural Products

*F. Cardona, C. Parmeggiani, E. Faggi, C. Bonaccini, P. Gratteri, L. Sim, T. M. Gloster, S. Roberts, G. J. Davies, D. R. Rose, A. Goti** 1627–1636

Total Syntheses of Casuarine and Its 6-*O*- α -Glucoside: Complementary Inhibition towards Glycoside Hydrolases of the GH31 and GH37 Families

Shape-persistent micelles consisting of exactly 12 molecules (see picture), which coexist with rodlike micelles, are formed by the self-labeled amphicalixarene at pH 7. In contrast to other examples of structurally defined micelles, this new type of amphiphile serves as a fluorescence reporter and provides an extended cavity structure in the hydrophilic part, thereby facilitating the inclusion of guest molecules.

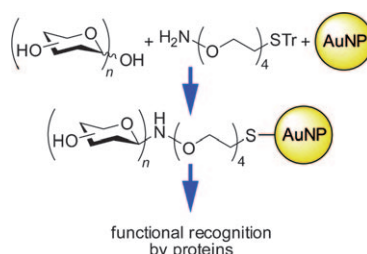


Micelles

M. S. Becherer, B. Schade, C. Böttcher, A. Hirsch** 1637–1648

Supramolecular Assembly of Self-Labeled Amphicalixarenes

Open or closed: *N*-Glycosyl oxime versus open-chain glycosyl oxime is the key to protein recognition on glycananoparticles. Unprotected glycans are captured by oxime formation with a novel bifunctional reagent and the resulting glycan-linker conjugates are anchored to gold nanoparticles (AuNPs). These glycananoparticles maintain the structural integrity of glycans in the study of protein–carbohydrate interactions (see figure).



Glycananoparticles

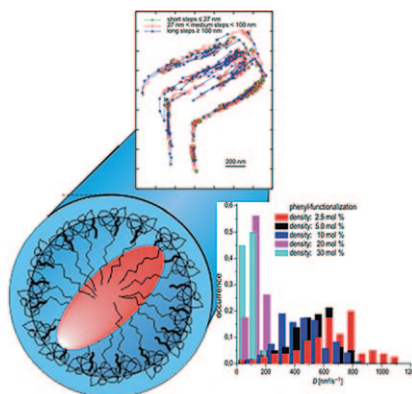
*M. B. Thygesen, J. Sauer, K. J. Jensen** 1649–1660

Chemoselective Capture of Glycans for Analysis on Gold Nanoparticles: Carbohydrate Oxime Tautomers Provide Functional Recognition by Proteins

Single-Molecule Studies

T. Lebold, L. A. Mühlstein,
J. Blechinger, M. Riederer,
H. Amenitsch, R. Köhn, K. Peneva,
K. Müllen, J. Michaelis, C. Bräuchle,*
T. Bein* 1661–1672

Tuning Single-Molecule Dynamics in Functionalized Mesoporous Silica

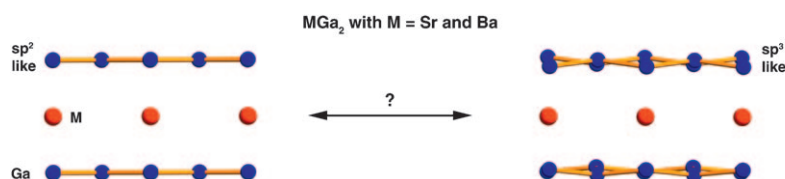


Diffusion of single molecules of a substituted terrylene diimide dye in functionalized mesoporous silica films was monitored by single-molecule fluorescence microscopy. By varying the chemical nature and density of the functional groups, the diffusion dynamics of the dye molecules can be controlled precisely. The picture shows a sketch of a dye molecule in a pore, diffusion data for different phenyl functionalization densities, and the trajectory of one molecule in a cyanopropyl-functionalized film.

Chemical Bonding

F. Haarmann,* K. Koch, D. Grüner,
W. Schnelle, O. Pecher, R. Cardoso-Gil,
H. Borrmann, H. Rosner,
Yu. Grin 1673–1684

Electronic Structure, Chemical Bonding, and Solid-State NMR Spectroscopy of the Digallides of Ca, Sr, and Ba



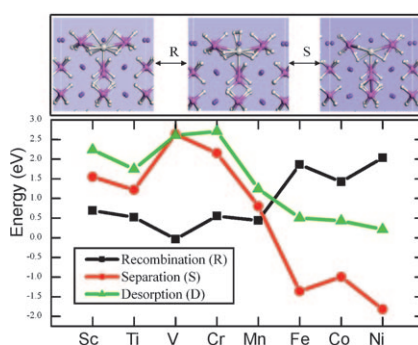
Delving into digallides: The characteristics of the chemical bonding of the digallides of the alkaline-earth metals (see figure) have been studied by application of experimental methods,

such as single-crystal X-ray diffraction and solid-state NMR spectroscopy, in combination with quantum mechanical calculations.

Hydrogen Storage

J. Liu, Y. Han, Q. Ge* 1685–1695

Effect of Doped Transition Metal on Reversible Hydrogen Release/Uptake from NaAlH₄

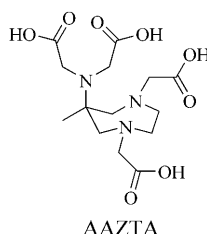


Storage facility: A dihydrogen complex formed in transition-metal-doped NaAlH₄ was found to play important roles in hydrogen release/uptake (see figure). Electronic structure analysis revealed that the electron transfer between hydrogen and Al groups was mediated by the d orbitals of transition metals. Hydrogen release/uptake from the transition-metal-doped NaAlH₄ was accompanied by an exchange of Al–H and H–H bond ligands through σ -bond metathesis.

Kinetic Stability

Zs. Baranyai, F. Uggeri,
G. B. Giovenzana, A. Bényei,
E. Brücher, S. Aime* 1696–1705

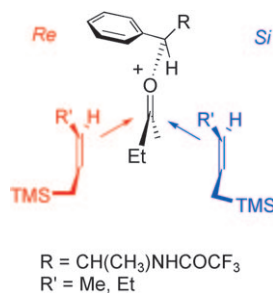
Equilibrium and Kinetic Properties of the Lanthanoids(III) and Various Divalent Metal Complexes of the Heptadentate Ligand AAZTA



Towards improved kinetic stability: A detailed account of the complexation properties of the ligand 1,4-bis(hydroxycarbonylmethyl)-6-[bis(hydroxycarbonylmethyl)]amino-6-methylperhydro-1,4-diazepine (AAZTA; see figure) is reported. Its Gd³⁺ complex shows a kinetic stability superior to that of complexes formed by higher denticity ligands and opens the way for a new reference structure for MRI contrast agents.

The solvent makes the difference:

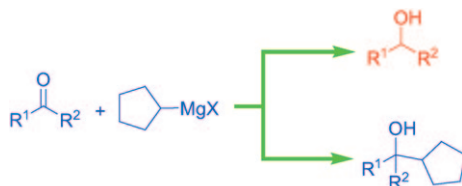
While attack at the *Re* face of the intermediate oxocarbenium ion becomes less energy demanding with increasing size of *R'*, it is the solvent effect that makes this attack the main trajectory, leading to inversed stereochemistry (see picture).



Domino Ketone Allylations

L. F. Tietze, T. Kinzel,
S. Schmatz* 1706–1712

Stereoselective Allylation of Ketones: Explanation for the Unusual Inversion of the Induced Stereochemistry in the Auxiliary-Mediated Crotylation and Pentenylation of Butanone by DFT Calculations



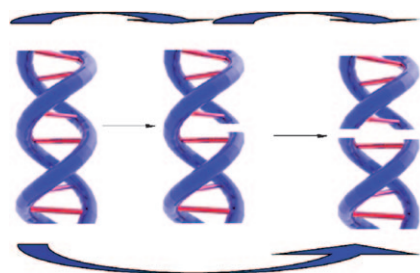
Tuning in: The reaction of halocyclopentane organometallic reagents can be tuned by the choice of metal (see scheme). Cyclopentylmagnesium bromide reduces aldehydes and ketones to the corresponding alcohols. However,

in the presence of ZnCl_2 , normal Grignard addition to the ketones gives tertiary alcohols with complete diastereoselectivity. These protocols were used in the asymmetric synthesis of two medicinally important compounds.

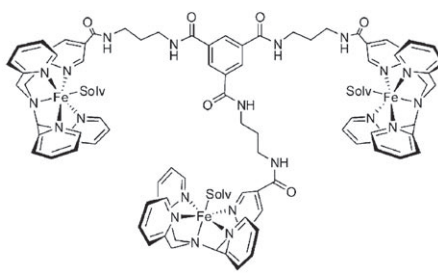
Asymmetric Synthesis

*S. Roy, A. Sharma, S. Mula,
S. Chattopadhyay** 1713–1722

Metal-Dependent Reaction Tuning with Cyclopentylmetal Reagents: Application to the Asymmetric Synthesis of (+)- α -Conhydrine and (S)-2-Cyclopentyl-2-phenylglycolic Acid



Bleomycin mimics: Efficient oxidative double-strand DNA cleavage has been achieved with multinuclear non-heme iron complexes (see scheme). These

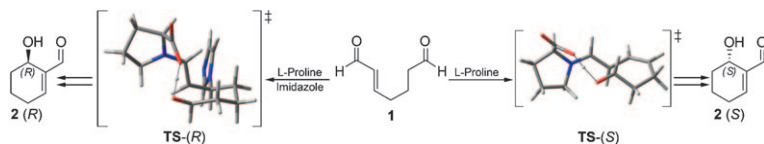


complexes therefore represent model compounds that mimic the mode of action of the anti-tumor drug bleomycin.

DNA Cleavage

*R. P. Megens, T. A. van den Berg,
A. D. de Bruijn, B. L. Feringa,*
G. Roelfes** 1723–1733

Multinuclear Non-Heme Iron Complexes for Double-Strand DNA Cleavage



A rationalization of stereoselectivity:

The mechanisms of proline-catalyzed and imidazole-co-catalyzed intramolecular Baylis–Hillman reactions have been studied by using density functional theory methods. The computational data has allowed us to rational-

ize the experimental outcome, validating some of the mechanistic steps proposed in the literature, as well as to propose new ones that considerably change and improve our understanding of the full reaction path (see scheme).

Asymmetric Catalysis


*F. J. S. Duarte, E. J. Cabrita,
G. Frenking, A. G. Santos** 1734–1746

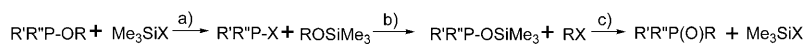
Density Functional Study of Proline-Catalyzed Intramolecular Baylis–Hillman Reactions



Organophosphorus Chemistry

W. Dabkowski,* A. Ozarek,
S. Olejniczak, M. Cypryk,
J. Chojnowski,
J. Michalski* 1747–1756

 **Studies on the Efficient Generation of Phosphorus–Carbon Bonds via a Rearrangement of P^{III} Esters Catalysed by Trimethylhalosilanes**




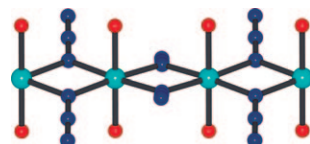
Unprecedented C–P systems: Me₃SiX (X = Br, I) catalyses rearrangements of P^{III} esters R'R''P–OR into the corresponding phosphoryl systems, providing a simple, mild and efficient route

to a variety of structures containing P–C bonds. The mechanism has been found to be fundamentally different from that of the Arbuzov–Michaelis reaction and includes three definite steps a, b and c (see scheme).

Magnetic Materials

H.-L. Sun, Z.-M. Wang,*
S. Gao* 1757–1764

 **[M(N₃)₂(H₂O)₂](bpeado): Unusual Antiferromagnetic Heisenberg Chain (M = Mn) and Ferromagnetic Ising Chain (M = Co) with Large Coercivity and Magnetic Relaxation (bpeado = 1,2-Bis(4-pyridyl)ethane-*N,N'*-dioxide)**

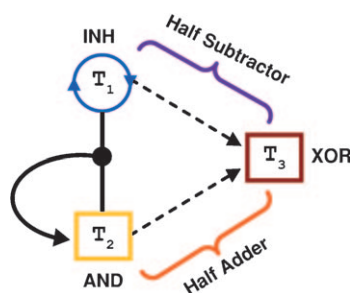


Contrasting magnetic properties: Two isostructural metal-azido magnetic chains embedded in 3D threefold interpenetrated H-bonded frameworks and separated by a long bpeado spacer have been assembled (see figure). Incorporation of Mn²⁺ displays a rarely observed antiferromagnetic Heisenberg chain, while incorporation of Co²⁺ displays a ferromagnetic Ising chain.

Logic Gates

N. Wagner, G. Ashkenasy* 1765–1775


Systems Chemistry: Logic Gates, Arithmetic Units, and Network Motifs in Small Networks

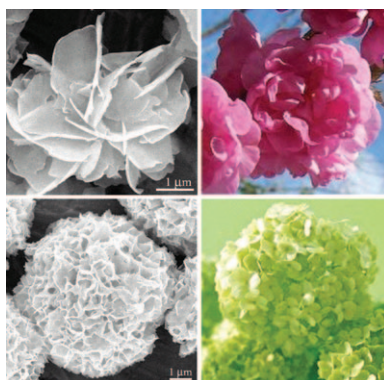


How much “systems chemistry” really exists within small networks? To answer this question, the authors study tertiary networks that facilitate molecular replication through all Boolean logic operations and show how such gates can be wired together to perform computational and feed-forward based network motifs (see graphic).

Nanostructures


L. Zhou, W. Wang,* H. Xu, S. Sun,
M. Shang 1776–1782


 **Bi₂O₃ Hierarchical Nanostructures: Controllable Synthesis, Growth Mechanism, and their Application in Photocatalysis**




Flower power: Unique 3D flower-like Bi₂O₃ hierarchical nanostructures were synthesized using a mild aqueous template-free method (see figure). By introducing VO₃[−] into the reaction system, which mediated the nucleation and growth of Bi₂O₃, the in situ self-assembly of 3D hierarchitectures from 2D nanosheets has been realized.

* Author to whom correspondence should be addressed

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

 Full Papers labeled with this symbol have been judged by two referees as being “very important papers”.

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

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Issue 6/2009 was published online on January 20, 2009

CORRIGENDUM

N. Bisek, S. Wetzel, H.-D. Arndt,
H. Waldmann 8847–8860

**Synthesis and Conformational Analysis
of Stevastelin C3 Analogues and Their
Activity Against the Dual-Specific
Vaccina H1-Related Phosphatase**

Chem. Eur. J., 2008, 14

DOI: 10.1002/chem.200800692

In the paper by H. Waldmann, H.-D. Arndt et al., the entry for compound **29** in Table 3 has been found to list the stereochemical compound assignment wrongly. The correct descriptors for compound **29** in Table 3 should read 2*S*,3*R*,4*S*. The authors apologize for this oversight and confirm that it does not affect any of the hypotheses or conclusions delineated in the original paper.

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As an Associate Editor you will be responsible for peer-review procedures and the acquisition of journal content. This will involve close interaction with Editorial Board members as well as with authors and referees from all over the world, and representing the journal at international conferences. In addition, you will be involved in all aspects of the editing and publishing process.

Applicants for this position should have a broad interest in chemistry, be self-motivated, have excellent organizational and communication skills (written and verbal), be diplomatic, flexible, familiar with text and graphics computer applications, and have an excellent command of the English language. Fluency in German and previous publishing experience would be advantageous.

The Editorial Office is based at WILEY-VCH in Weinheim, a lively small town within short distance of the vibrant urban centres of Heidelberg and Mannheim in southwest Germany. Applicants should send their full CV with a covering letter describing their suitability for the post to:

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