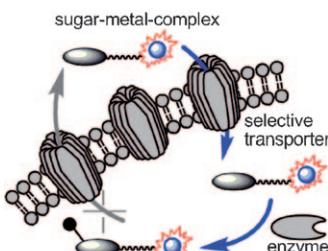


# CONCEPTS

## Bioinorganic Chemistry

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

### Prospects of Metal Complexes Peripherally Substituted with Sugars in Biomedicinal Applications



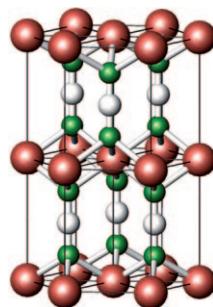
**Sugar is good for you!** The latest developments in the field of sugar substitution of metal complexes and its influence on the action of these complexes in biological systems are discussed (see figure). In particular, the progress in applications as selective tracers and therapeutics in connection 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)<sub>2</sub>: Synthesis, Structure, and Magnetic Properties of a Nitrogen-Based Pseudo-oxide and -hydroxide of Divalent Iron

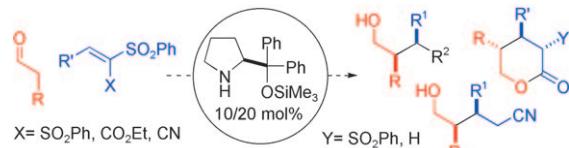


**Iron man challenge:** Iron carbodiimide, FeNCN, and its precursor iron (bis)-monohydrocyanamide, Fe(NCNH)<sub>2</sub>, have been synthesized and physically characterized. Both FeNCN and Fe(NCNH)<sub>2</sub> exhibit nitrogen-mediated antiferromagnetic superexchange interactions with reduced magnetic 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



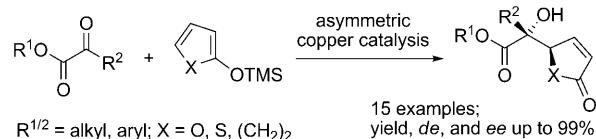
**Joined together**, organocatalysts aldehydes and sulfones: A diaryl prolinol silyl ether was found to catalyse efficiently and enantioselectively the con-

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

## Asymmetric Catalysis

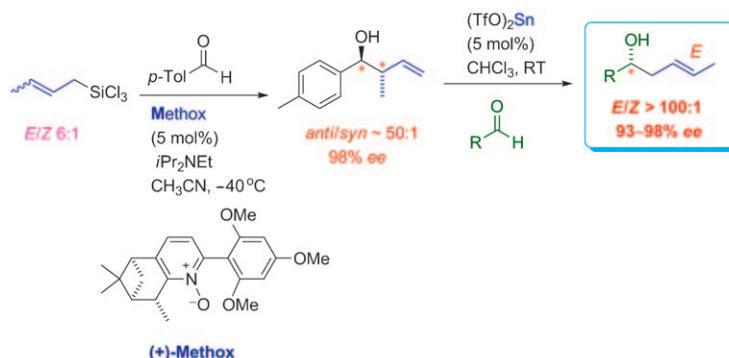
M. Frings, I. Atodiresei, J. Runsink,  
G. Raabe, C. Bolm\* ..... 1566–1569

### Catalyzed Vinylogous Mukaiyama Aldol Reactions with Controlled Enantio- and Diastereoselectivities



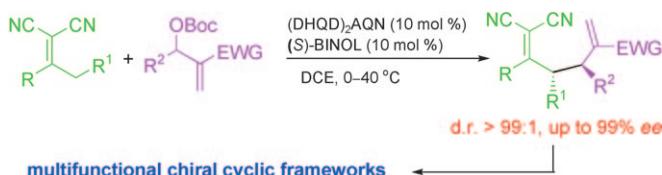
**In control:** A new catalytic vinylogous Mukaiyama aldol reaction provides products with high diastereo- and enantioselectivities (up to 99% *de* and *ee*; see scheme). The relative and abso-

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  $\alpha$ -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.



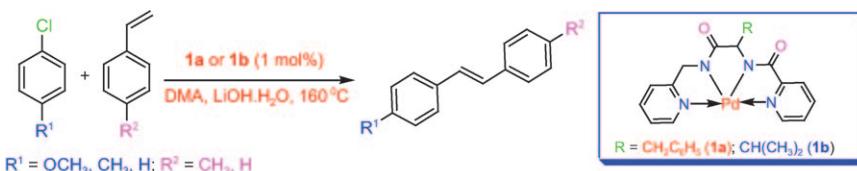
**The first highly enantioselective allylic-allylic alkylation** of  $\alpha,\alpha$ -dicyanoalkenes and Morita–Baylis–Hillman carbonates by dual catalysis of  $(DHQD)_2AQN$  and  $(S)$ -BINOL has been investigated. Excellent stereoselectivities have been achieved for a broad spectrum of substrates (d.r.

> 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-diyi) 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  $\alpha$ -Crotylation of Aldehydes with a Kinetic Self-Refinement of Stereochemistry



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

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

## Organocatalysis

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

**Dual Organocatalysis: Asymmetric Allylic–Allylic Alkylation of  $\alpha,\alpha$ -Dicyanoalkenes and Morita–Baylis–Hillman Carbonates**



## C–C Coupling

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

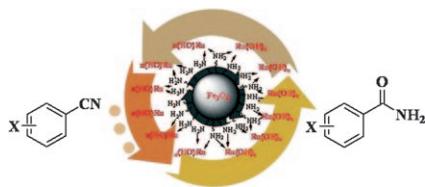
**N4-Tetradeinate Dicarboxyamide/Dipyridyl Palladium Complexes as Robust Catalysts for the Heck Reaction of Deactivated Aryl Chlorides**



**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**



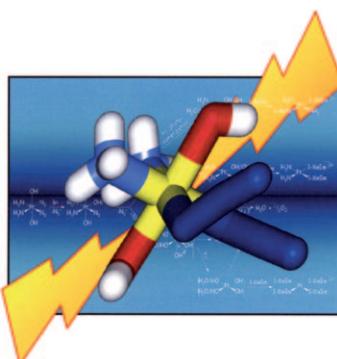
**Magnetic attraction not filtration:** A magnetic nanoparticle-supported ruthenium hydroxide catalyst (see figure) was readily prepared from inexpensive starting materials and shown to catalyze the hydration of nitriles with excellent yield in a benign aqueous medium. Catalyst recovery using an external 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<sup>IV</sup>(N<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] with 1-Methylimidazole**

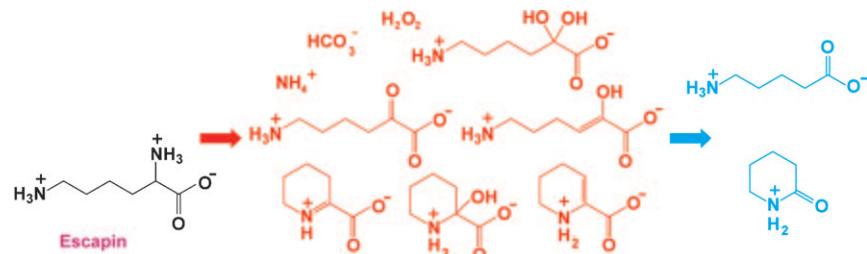


**Lighting up new platinum anticancer complexes:** Photoactivation of a platinum(IV) diazido anticancer complex in the presence of a derivative of imidazole, an important constituent of biomolecules, gives surprising photo-products, including a tetrakis imidazole platinum(II) adduct (see figure), together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



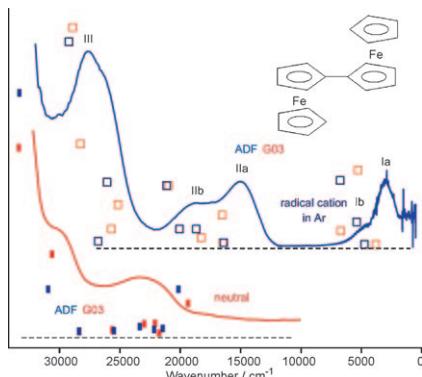
**A complex mixture** of products in an enzymatic reaction: *Aplysia californica* releases amino acid oxidase and its

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

**Mixed-Valent Compounds**

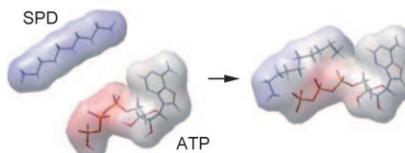
R. Warratz, H. Aboulfadil, T. Bally,\*  
F. Tuczek\* ..... 1604–1617

 **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<sup>II</sup>-Fe<sup>III</sup> 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<sup>II</sup>-Fe<sup>III</sup> radical cation.

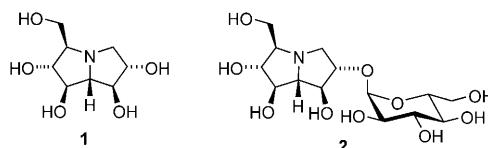
**A complex rotation:** The solution conformation of spermidine (SPD) was elucidated by using diastereospecifically deuterated and  $^{13}\text{C}$ -labeled derivatives to diagnose the orientation of seven conformationally relevant bonds. NMR coupling constants were determined for a complex formed from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

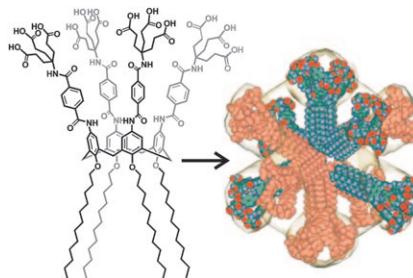
### Conformational Change of Spermidine upon Interaction with Adenosine Triphosphate in Aqueous Solution



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

**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.



### 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

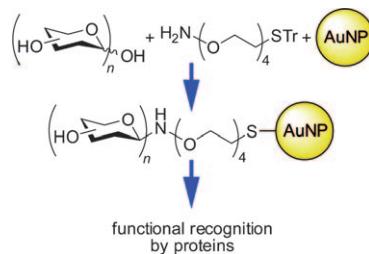
### Total Syntheses of Casuarine and Its 6- $O$ - $\alpha$ -Glucoside: Complementary Inhibition towards Glycoside Hydrolases of the GH31 and GH37 Families

### Micelles

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

### Supramolecular Assembly of Self-Labeled Amphicalixarenes

**Open or closed:** *N*-Glycosyl oxyamine versus open-chain glycosyl oxime is the key to protein recognition on glyconanoparticles. 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 glyconanoparticles maintain the structural integrity of glycans in the study of protein–carbohydrate interactions (see figure).



### Glyconanoparticles

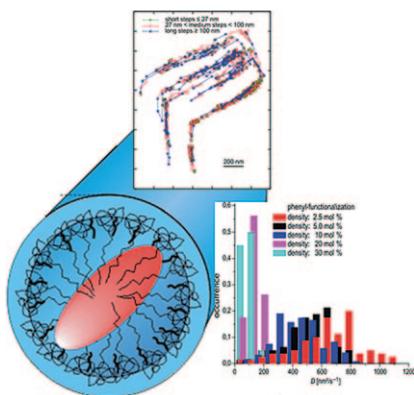
*M. B. Thygesen, J. Sauer, K. J. Jensen\** ..... 1649–1660

### 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**

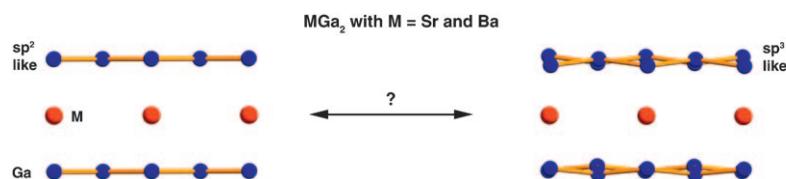


**Diffusion of single molecules** of a substituted terrylene diimide dye in functionalized mesoporous silica films was monitored by single-molecule fluorescence microscopy. By varying the chemical nature and density of the functional groups, the diffusion dynamics of the dye molecules can be controlled 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. Borrman, H. Rosner,  
Yu. Grin ..... 1673–1684

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



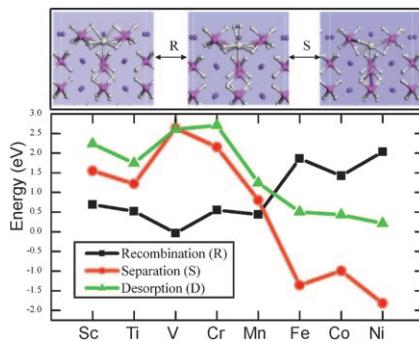
**Delving into digallides:** The characteristics of the chemical bonding of the digallides of the alkaline-earth metals (see figure) have been studied by application of experimental methods,

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 NaAlH<sub>4</sub>**

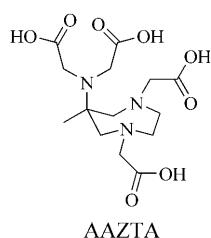


**Storage facility:** A dihydrogen complex formed in transition-metal-doped NaAlH<sub>4</sub> was found to play important roles in hydrogen release/uptake (see figure). Electronic structure analysis revealed that the electron transfer between hydrogen and Al groups was mediated by the d orbitals of transition metals. Hydrogen release/uptake from the transition-metal-doped NaAlH<sub>4</sub> was accompanied by an exchange of Al–H and H–H bond ligands through  $\sigma$ -bond metathesis.

**Kinetic Stability**

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

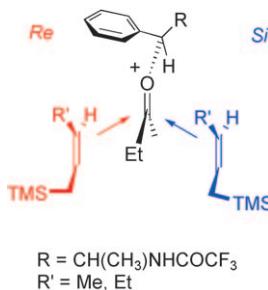
 **Equilibrium and Kinetic Properties of the Lanthanoids(III) and Various Divalent Metal Complexes of the Heptadentate Ligand AAZTA**



**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 Gd<sup>3+</sup> 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:

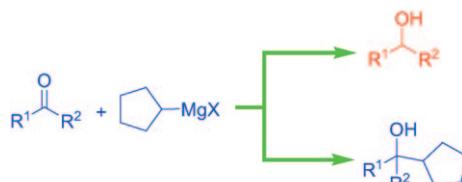
While attack at the *Re* face of the intermediate oxocarbenium ion becomes less energy demanding with increasing size of  $R'$ , it is the solvent effect that makes this attack the main trajectory, leading to inverted stereochemistry (see picture).



## Domino Ketone Allylations

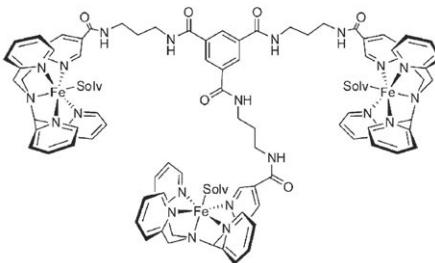
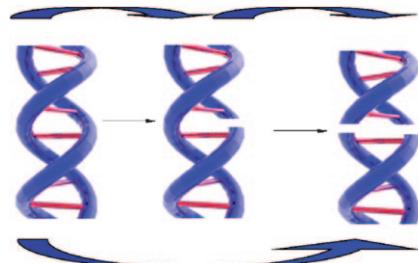
L. F. Tietze,\* T. Kinzel,  
S. Schmatz ..... 1706–1712

**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**



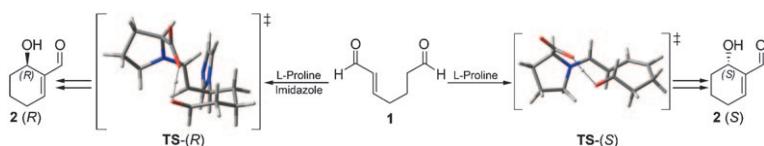
**Tuning in:** The reaction of halocyclopentane organometallic reagents can be tuned by the choice of metal (see scheme). Cyclopentylmagnesium bromide reduces aldehydes and ketones to the corresponding alcohols. However,

in the presence of  $\text{ZnCl}_2$ , 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.



**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.



**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 Synthesis

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

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



## DNA Cleavage

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

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

## Asymmetric Catalysis

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

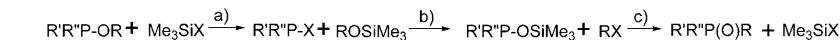
**Density Functional Study of Proline-Catalyzed Intramolecular Baylis–Hillman Reactions**



**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<sup>III</sup> Esters Catalysed by Trimethylhalosilanes**

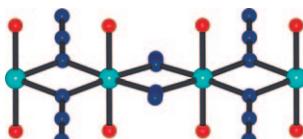


**Unprecedented C–P systems:**  $\text{Me}_3\text{SiX}$  ( $\text{X}=\text{Br}, \text{I}$ ) catalyses rearrangements of  $\text{P}^{\text{III}}$  esters  $\text{R}'\text{R}''\text{P}-\text{OR}$  into the corresponding phosphoryl systems, providing a simple, mild and efficient route

to a variety of structures containing  $\text{P}-\text{C}$  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



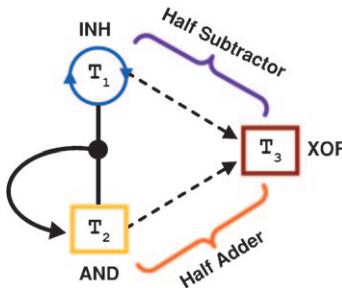
**$[\text{M}(\text{N}_3)_2(\text{H}_2\text{O})_2]\cdot(\text{bpeado})$ : Unusual Antiferromagnetic Heisenberg Chain ( $\text{M}=\text{Mn}$ ) and Ferromagnetic Ising Chain ( $\text{M}=\text{Co}$ ) with Large Coercivity and Magnetic Relaxation ( $\text{bpeado}=1,2\text{-Bis}(4\text{-pyridyl})\text{ethane-}N,N'\text{-dioxide}$ )**

**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  $\text{Mn}^{2+}$  displays a rarely observed antiferromagnetic Heisenberg chain, while incorporation of  $\text{Co}^{2+}$  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**

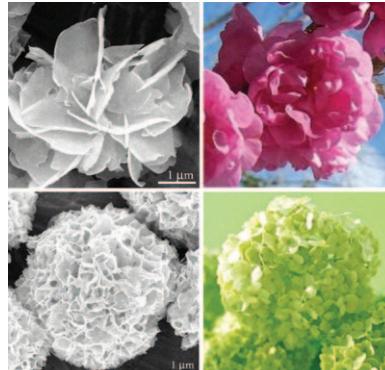


**How much “systems chemistry” really exists within small networks?** To answer this question, the authors study tertiary networks that facilitate molecular replication through all Boolean logic operations and show how such gates can be wired together to perform computational and feed-forward based network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

**Nanostructures**

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

**$\text{Bi}_2\text{O}_3$  Hierarchical Nanostructures: Controllable Synthesis, Growth Mechanism, and their Application in Photocatalysis**



**Flower power:** Unique 3D flower-like  $\text{Bi}_2\text{O}_3$  hierarchical nanostructures were synthesized using a mild aqueous template-free method (see figure). By introducing  $\text{VO}_3^-$  into the reaction system, which mediated the nucleation and growth of  $\text{Bi}_2\text{O}_3$ , the *in situ* self-assembly of 3D hierarchitectures from 2D nanosheets has been realized.

\* Author to whom correspondence should be addressed

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

Supporting information 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

Spotlights **1544** Authors **1784** Keywords **1785** Preview **1787**

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

## CORRIGENDUM

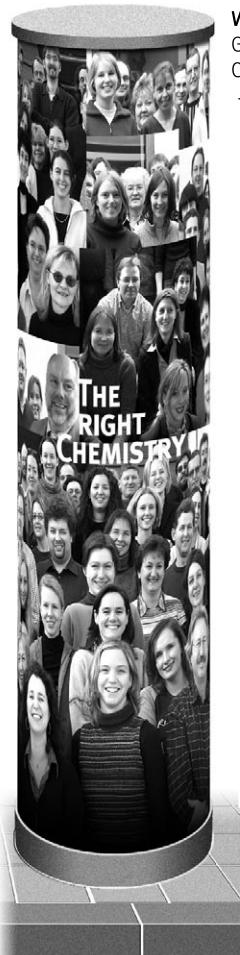
*N. Bisek, S. Wetzel, H.-D. Arndt,  
H. Waldmann* ..... 8847–8860

**Synthesis and Conformational Analysis  
of Stevastelin C3 Analogues and Their  
Activity Against the Dual-Specific  
Vaccinia 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 *2S,3R,4S*. 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.

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