



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](http://www.angewandte.org) soon:

H. Matsuzawa, Y. Miyake, Y. Nishibayashi\*

**Ruthenium-Catalyzed Enantioselective Propargylation of Aromatic Compounds with Propargylic Alcohols via Allenylidene Intermediates**

C. Fehr\*

**Catalytic, Enantioselective Tautomerization of Isolated Enols**

J. S. J. McCahill, G. C. Welch, D. W. Stephan\*

**Reactivity of Frustrated Lewis Pairs: Three-Component Reactions of Phosphine, Borane, and Olefins**

H. Braunschweig,\* M. Forster, K. Radacki, F. Seeler, G. R. Whittell  
**Stepwise Intermetal Borylene Transfer: Synthesis and Structure of Mono- and Dinuclear Co Borylene Complexes**

A. Scarso,\* L. Pellizzaro, O. De Lucchi, A. Linden, F. Fabris\*  
**Gas Hosting in Enantiopure Self-Assembled Oximes**

S. Wittrock, T. Becker, H. Kunz\*

**Synthetic Vaccines from Tumor-Associated Glycopeptide Antigens by Immunocompatible Linking to Bovine Serum Albumin through Thioether Formation**

Frank Albert Cotton (1930–2007)

Metal-Catalysis in Industrial Organic Processes

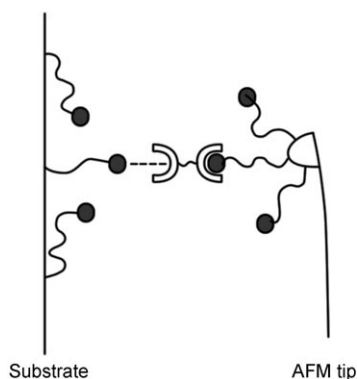
Gian Paolo Chiusoli, Peter M. Maitlis

## Obituary

J. P. Fackler, Jr. \_\_\_\_\_ 3790

## Books

reviewed by L. J. Goofsen \_\_\_\_\_ 3791



**The power of the Force:** The rupture force of supramolecular bonds, as well as the unbinding dynamics of associated polymers, have been studied by AFM-based single-molecule force spectroscopy (AFM-SMFS). The first quantitative comparison of bond-rupture dynamics from independent AFM-SMFS and NMR data is highlighted.

## Highlights

### Supramolecular Chemistry

G. J. Vancso\* \_\_\_\_\_ 3794–3796

Feeling the Force of Supramolecular Bonds in Polymers



**All this talk of water:** Aqueous-based organocatalytic processes involve a complex set of parameters, and a holistic approach is the key to making informed decisions on the benefits on a case-by-case basis. A fundamental mechanistic understanding of the role of water in any reaction is necessary before its general use in organocatalytic reactions may be advocated. Copyright of the picture (water drops 1): Adam Hart-Davis.

## Essays

### Organocatalysis

D. G. Blackmond,\* A. Armstrong, V. Coombe, A. Wells \_\_\_\_\_ 3798–3800

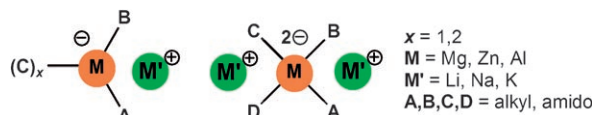
Water in Organocatalytic Processes: Debunking the Myths

## Reviews

### Organometallic Reagents

R. E. Mulvey,\* F. Mongin,\* M. Uchiyama,\*  
Y. Kondo\* ————— **3802–3824**

Deprotonative Metalation Using Ate  
Compounds: Synergy, Synthesis, and  
Structure Building



**Crazy ates:** Metalations of organic sub-  
strates with alkali-metal magnesiates,  
zincates, and aluminates have opened up  
new perspectives in synthetic and struc-  
tural chemistry. This Review covers selec-

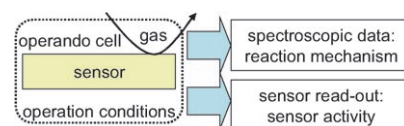
ted syntheses made possible by applica-  
tion of such “ate” complexes as deproto-  
nation reagents, together with insight into  
synergetic effects in the syntheses of these  
species.

### Gas Sensors

A. Gurlo,\* R. Riedel ————— **3826–3848**

In Situ and Operando Spectroscopy for  
Assessing Mechanisms of Gas Sensing

**On the job:** What previously seemed  
impossible, such as monitoring of the  
processes on working gas sensors, is now  
possible. Physicochemical processes on  
an active sensor can be studied under  
working conditions and in real time (see  
scheme). This Review covers the in situ  
and operando methodology for studying  
the gas-sensing mechanism on semicon-  
ducting metal oxides.



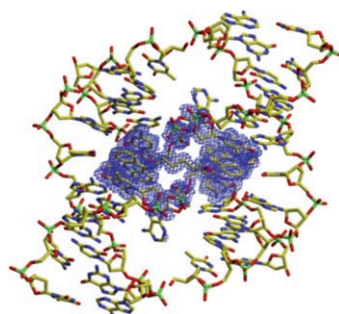
## Communications

### DNA Structures

A. L. Brogden, N. H. Hopcroft, M. Searcey,  
C. J. Cardin\* ————— **3850–3854**



Ligand Bridging of the DNA Holliday  
Junction: Molecular Recognition of a  
Stacked-X Four-Way Junction by a Small  
Molecule



**Planning a Holiday:** A new mode of  
binding to a stacked-X, four-way Holliday  
junction is described in which a chromo-  
phore molecule binds across the center of  
the junction and two adenine residues are  
replaced by the acridine chromophores at  
either side of the crossover. This binding  
mode is specific for the Holliday junction  
and does not cause unwinding of the DNA  
helices.

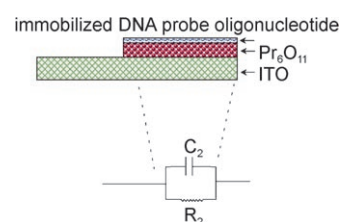
### DNA Probes

S. Shrestha, C. M. Y. Yeung, C. E. Mills,  
J. Lewington,  
S. C. (Edman) Tsang\* ————— **3855–3859**



Chemically Immobilized Single-Stranded  
Oligonucleotides on Praseodymium  
Oxide Nanoparticles as an Unlabeled  
DNA Sensor Probe Using Impedance

**A spark of attraction:** Ellipsoidal  $\text{Pr}_6\text{O}_{11}$   
particles on indium tin oxide (ITO) mod-  
ified with single-stranded oligonucleo-  
tides act as an unlabeled DNA probe.  
Upon recognition of complementary  
bases in solution, an impedance change  
(capacitance change) is detected. An  
equivalent impedance change is not  
obtained upon the addition of an oligo-  
nucleotide with slightly mismatched  
bases.

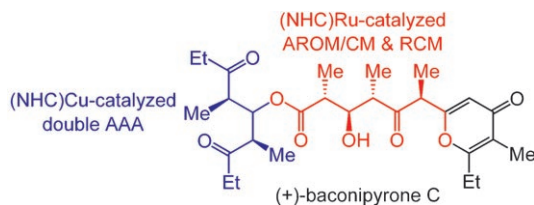


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**Chiral carbenes as major players:** Two recently discovered chiral N-heterocyclic carbene (NHC) complexes play a crucial role in a concise enantioselective total synthesis of baconipyron C (see scheme). An (NHC)Cu complex catalyzes

a double asymmetric allylic alkylation (AAA), and an (NHC)Ru complex catalyzes an asymmetric ring-opening/cross-metathesis (AROM/CM) to establish the absolute configuration of the target. RCM = ring-closing metathesis.

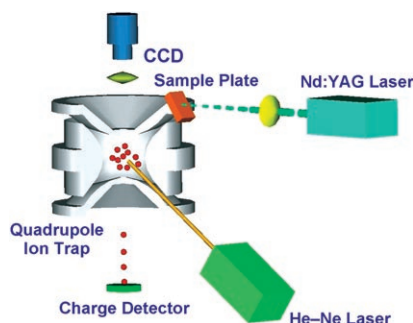
## Natural Products

D. G. Gillingham,  
A. H. Hoveyda\* — 3860–3864

Chiral N-Heterocyclic Carbenes in Natural Product Synthesis: Application of Ru-Catalyzed Asymmetric Ring-Opening/Cross-Metathesis and Cu-Catalyzed Allylic Alkylation to Total Synthesis of Baconipyron C



**Mass exodus:** A mass spectrometer for the rapid measurement of mass distributions of cells and microparticles is described. A discharge process is used to provide cells with thousands of charges so that direct charge measurement can be achieved. This device was used to measure microparticles with masses as high as  $10^{15}$  Da and to distinguish cancer cells from normal cells.

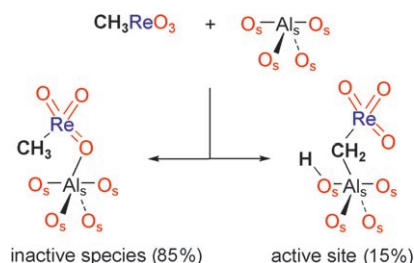


## Mass Spectrometry

W.-P. Peng, H.-C. Lin, H.-H. Lin, M. Chu,  
A. L. Yu, H.-C. Chang,  
C.-H. Chen\* — 3865–3869

Charge-Monitoring Laser-Induced Acoustic Desorption Mass Spectrometry for Cell and Microparticle Mass Distribution Measurement

**A minor species,** generated by C–H activation of the methyl group of  $\text{CH}_3\text{ReO}_3$  on reactive surface sites of alumina, is the active site of alumina-supported  $\text{CH}_3\text{ReO}_3$ , a highly active olefin metathesis catalyst, while the major species, formed by coordination of  $\text{CH}_3\text{ReO}_3$  at the same sites, is inactive (see scheme;  $\text{O}_s$  denotes the O atoms of the alumina surface).



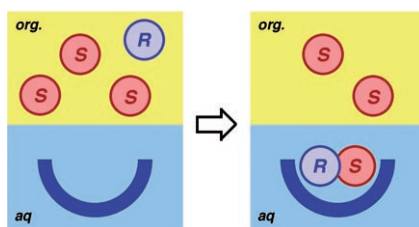
## Metathesis Catalysts

A. Salameh, J. Joubert, A. Baudouin,  
W. Lukens, F. Delbecq, P. Sautet,\*  
J. M. Basset,\* C. Copéret\* — 3870–3873

$\text{CH}_3\text{ReO}_3$  on  $\gamma\text{-Al}_2\text{O}_3$ : Understanding Its Structure, Initiation, and Reactivity in Olefin Metathesis



**A bowl of pairs:** The water-soluble bowl-shaped coordination compound formed from  $[\text{Pd}(\text{en})(\text{NO}_3)_2]$  (en = ethylenediamine) and tris(3-pyridyl)triazine recognizes preferentially a racemic pair of guest molecules such as 1,1'-bi-2-naphthol. This bimolecular recognition results in chirality enrichment in the organic phase without the need to add another source of chirality (see scheme).



## Molecular Recognition

M. Yoshizawa, M. Tamura,  
M. Fujita\* — 3874–3876

Chirality Enrichment through the Heterorecognition of Enantiomers in an Achiral Coordination Host





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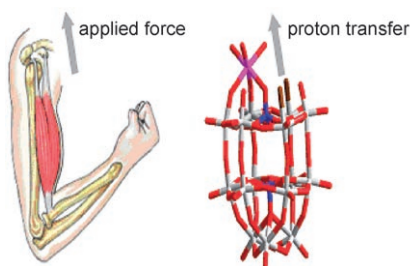
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**Back and forth:** The two complexes  $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$  and  $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr\{P_2W_{17}O_{61}\}]^{14-}$  exhibit extensive dynamic structural changes induced by completely reversible multiple protonation behavior, comparable to the flexing of a muscle (see picture). The pH titration of the former complex indicates a two-step dissociation of all eight protons, in agreement with the structural and spectroscopic studies.

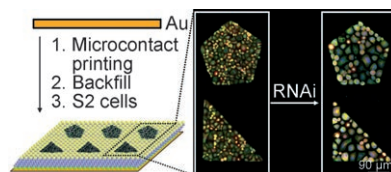
### Polyoxometalates

X. Fang, C. L. Hill\* — 3877–3880

Multiple Reversible Protonation of Polyoxoanion Surfaces: Direct Observation of Dynamic Structural Effects from Proton Transfer



**A good combination:** RNA interference (RNAi) technology combined with surface chemistry can be used to control RNAi-mediated gene silencing in *Drosophila* Schneider 2 (S2) cells patterned on tailored self-assembled monolayers of alkanethiolates on gold. The cell population and not the cell confluence was shown to be critical for the effectiveness of RNAi Rho GTPase.



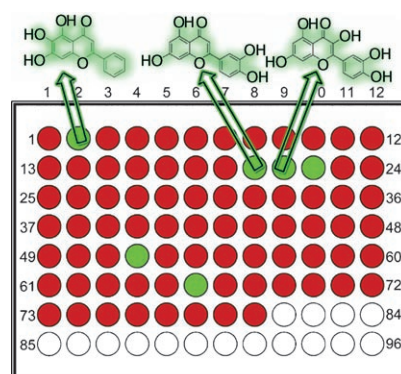
### RNA Interference

E. W. L. Chan, M. N. Yousaf\* — 3881–3884

Surface-Chemistry Control To Silence Gene Expression in *Drosophila* Schneider 2 Cells through RNA Interference



**Mutant exposed!** The synthetic utility of glycosynthase mutant enzymes has been expanded to allow the use of lipophilic acceptors, such as flavonoids, at rates comparable with those of natural glycosyltransferases. Sequential biocatalysis allows access to both di- and monosaccharide-modified products as well as natural product glycoflavonoids.



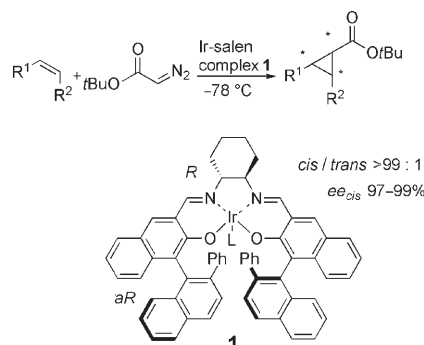
### Biocatalysis

M. Yang, G. J. Davies,\* B. G. Davis\* — 3885–3888

A Glycosynthase Catalyst for the Synthesis of Flavonoid Glycosides



**Ring the changes:** Iridium(III)–salen complexes **1** bearing a  $\sigma$ -coordinated aryl ligand ( $L = CH_3C_6H_4$ ,  $C_6H_5$ ) at the apical position are found to efficiently catalyze the *cis*- and enantioselective cyclopropanation of mono- and disubstituted olefins (see scheme).



### Cyclopropanation

S. Kanchiku, H. Suematsu, K. Matsumoto, T. Uchida, T. Katsuki\* — 3889–3891

Construction of an Aryliridium–Salen Complex for Highly *cis*- and Enantioselective Cyclopropanations

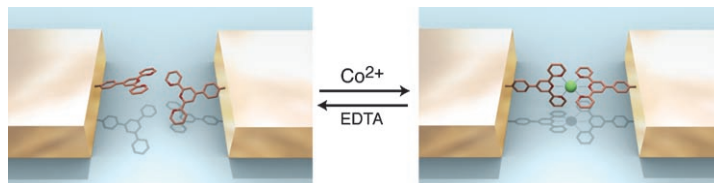


## Molecular Electronics

J. Tang, Y. Wang, J. E. Klare, G. S. Tulevski, S. J. Wind,\* C. Nuckolls\* — **3892–3895**



Encoding Molecular-Wire Formation within Nanoscale Sockets



**Wire straits:** Three-component molecular wires were constructed in situ by first assembling a monolayer of a bifunctional arene on the electrode surfaces, such that only one end of the molecule (thiol) reacts with the electrode. Then, a second mole-

cule was used to chemically bridge the gap between the termini of the films. Coordination chemistry in this context provides a versatile method to reversibly form molecular-scale wires (see picture). EDTA = ethylenediaminetetraacetate.

## Liquid Crystals

Y. Xu, S. Leng, C. Xue, R. Sun, J. Pan, J. Ford, S. Jin\* — **3896–3899**



A Room-Temperature Liquid-Crystalline Phase with Crystalline  $\pi$  Stacks

**Well stacked:** A liquid-crystalline material with crystalline  $\pi$  stacks has been synthesized in which the room-temperature liquid-crystalline phase consists of alternating 2D-crystalline mesogen layers and liquidlike alkyl layers. A long-range ordered layer structure forms as a consequence of the resulting microsegregation (see picture), with the  $\pi$  stacks contributing to the 2D crystalline order that exists within a layer.

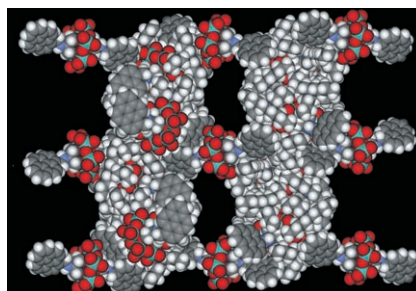


## Porous Materials

Y.-F. Song, D.-L. Long, L. Cronin\* — **3900–3904**



Noncovalently Connected Frameworks with Nanoscale Channels Assembled from a Tethered Polyoxometalate–Pyrene Hybrid



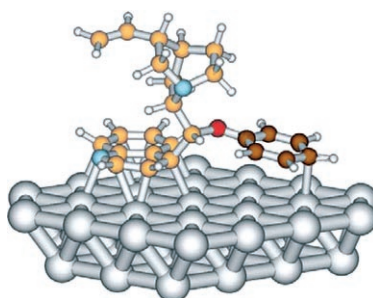
**Porous POMs:** Crystallization of a manganese-Anderson-type polyoxometalate (POM) derivatized with two pyrene moieties in the presence of tetrabutylammonium cations produces a nanoporous material with butterfly-shaped channels (O red, Mo green, C black, H white, N blue). The network is held together by very weak C–H...O=Mo interactions, but is stable to 240°C and can absorb up to 12 wt% chlorobenzene.

## Chiral Metal Surfaces

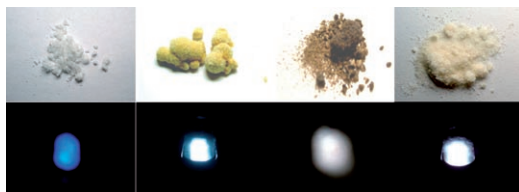
A. Vargas, D. Ferri, N. Bonalumi, T. Mallat, A. Baiker\* — **3905–3908**



Controlling the Sense of Enantioselection on Surfaces by Conformational Changes of Adsorbed Modifiers



**Shapeshifting:** The sense of enantioselection in the asymmetric hydrogenation of activated ketones over modified platinum depends on the cinchona-alkaloid modifier (for example, *O*-phenylcinchonidine; see picture). Spectroscopic and theoretical studies reveal that the chiral space is reshaped through a change in the conformation of the modifier.



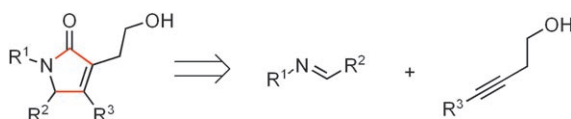
**Intrinsic white borate phosphors:** Solvothermal reaction of  $\text{H}_3\text{BO}_3$  and ethylenediamine afforded the first three-dimensional zeolite-like ammonium borate. Its blue photoluminescence can be modified to white by a simple heat-treatment

process at 250, at 360, or at 250 °C after doping with  $\text{Eu}^{3+}$  ions (see picture, left to right). In the absence of solvent, the same solvothermal reaction gave the first amine-pillared layer borate-based framework.

### White Phosphors

M.-S. Wang, G.-C. Guo,\* W.-T. Chen, G. Xu, W.-W. Zhou, K.-J. Wu, J.-S. Huang ————— 3909–3911

A White-Light-Emitting Borate-Based Inorganic–Organic Hybrid Open Framework



**In full control:** A regio- and stereoselective cross-coupling reaction between internal alkynes and imines that provides selective access to allylic amines and  $\gamma$ -lactams has been developed (see scheme). This inter-

molecular [2+2+1] process could be described as an alkoxide-directed aza-Pauson–Khand-like annulation. The alkyne can tolerate a wide range of substituents  $\text{R}^3$ .

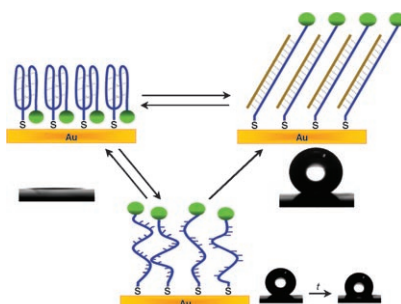
### Synthetic Methods

M. McLaughlin, M. Takahashi, G. C. Micalizio\* ————— 3912–3914

An Alkoxide-Directed Intermolecular [2+2+1] Annulation: A Three-Component Coupling Reaction for the Synthesis of Tetrasubstituted  $\alpha,\beta$ -Unsaturated  $\gamma$ -Lactams



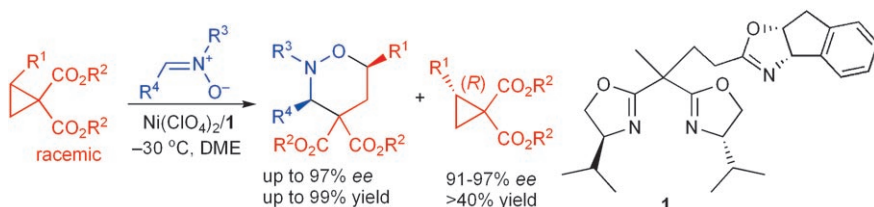
**Wet, wet, wet:** A responsive surface is presented that can switch between stable superhydrophilic, metastable superhydrophobic, and stable superhydrophobic states by an enthalpy-driven process (see picture). This macroscopic phenomenon of surface wettability originates from the coordinative effect of the collective nanoscale motion of DNA nanodevices and the surface microstructure.



### Surface Properties

S. Wang, H. Liu, D. Liu,\* X. Ma, X. Fang, L. Jiang\* ————— 3915–3917

Enthalpy-Driven Three-State Switching of a Superhydrophilic/Superhydrophobic Surface



**The multitasking catalyst 1**/ $\text{Ni}(\text{ClO}_4)_2$  mediates both title processes (see scheme). Together the efficient asymmetric cycloaddition and a kinetic resolution/cycloaddition provide access to both

enantiomers of tetrahydro-1,2-oxazines. DME = 1,2-dimethoxyethane;  $\text{R}^1$  = aryl, vinyl;  $\text{R}^2$  = Et, Me, benzyl;  $\text{R}^3$  = Me, Ph;  $\text{R}^4$  = aryl, styryl.

### Asymmetric Catalysis

Y.-B. Kang, X.-L. Sun, Y. Tang\* ————— 3918–3921

Highly Enantioselective and Diastereoselective Cycloaddition of Cyclopropanes with Nitrones and Its Application in the Kinetic Resolution of 2-Substituted Cyclopropane-1,1-dicarboxylates

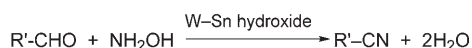
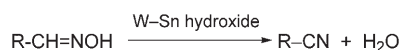


## Heterogeneous Catalysis

K. Yamaguchi, H. Fujiwara, Y. Ogasawara,  
M. Kotani, N. Mizuno\* — 3922–3925



A Tungsten–Tin Mixed Hydroxide as an Efficient Heterogeneous Catalyst for Dehydration of Aldoximes to Nitriles



**Mix and match:** A tungsten–tin mixed hydroxide (W–Sn hydroxide), prepared by the simple coprecipitation method, acts as a reusable heterogeneous catalyst for the dehydration of various aldoximes to the corresponding nitriles (see scheme,

top). Furthermore, the W–Sn hydroxide catalyst could be applied to the direct one-pot synthesis of nitriles from hydroxylamine and the corresponding aldehydes (see scheme, bottom).

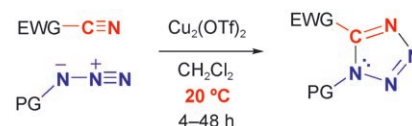
## Cu<sup>I</sup>-Catalyzed Cycloadditions

L. Bosch, J. Vilarrasa\* — 3926–3930



Cu<sub>2</sub>(OTf)<sub>2</sub>-Catalyzed and Microwave-Controlled Preparation of Tetrazoles from Nitriles and Organic Azides under Mild, Safe Conditions

**Avoiding hazards:** Cu<sub>2</sub>(OTf)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> (OTf = O<sub>3</sub>SCF<sub>3</sub>) is the catalyst of choice for the [3+2] cycloaddition of organic azides and ethyl cyanoformate or related nitriles (see scheme; PG = protecting group, EWG = electron-withdrawing group). For the first time, tetrazoles are obtained from these substrates at room temperature; heating at 80 °C in CH<sub>2</sub>Cl<sub>2</sub> (microwave reactor) is only required for the most reluctant substrates.

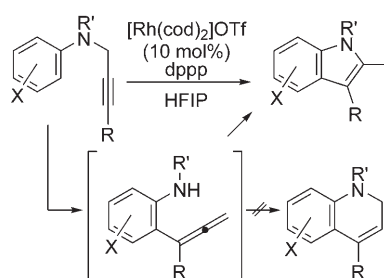


## Heterocycle Synthesis

A. Saito,\* A. Kanno,  
Y. Hanzawa\* — 3931–3933



Synthesis of 2,3-Disubstituted Indoles by a Rhodium-Catalyzed Aromatic Amino-Claisen Rearrangement of *N*-Propargyl Anilines



**Give me a ring!** A cationic Rh<sup>I</sup> catalyst promotes the formation of fused arenes containing a five-membered ring (see scheme) by an aromatic amino-Claisen rearrangement of *N*-propargyl aniline derivatives in refluxing hexafluoro-2-propanol (HFIP). cod = 1,5-cyclooctadiene, dppp = 1,3-bis(diphenylphosphanyl)propane, Tf = trifluoromethanesulfonyl.

## Asymmetric Enzyme Catalysis

M. Hall, C. Stueckler, W. Kroutil,  
P. Macheroux, K. Faber\* — 3934–3937



Asymmetric Bioreduction of Activated Alkenes Using Cloned 12-Oxophytodienoate Reductase Isoenzymes OPR-1 and OPR-3 from *Lycopersicon esculentum* (Tomato): A Striking Change of Stereoselectivity

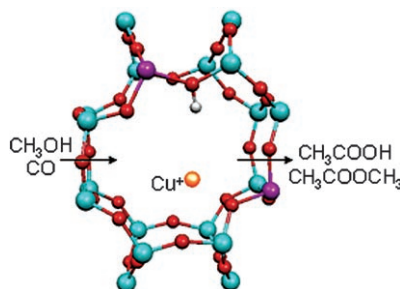


EWG = activating (electron-withdrawing) group

**Tomato source:** 12-Oxophytodienoate reductase isoenzymes OPR1 and OPR3 from tomato possess a broad substrate spectrum for the asymmetric bioreduction of  $\alpha,\beta$ -unsaturated enals, enones, dicarboxylic acids, and *N*-substituted maleimides (see scheme). Stereocomplementary behavior of both isoenzymes was observed in the reduction of a nitroalkene that led to the formation of opposite stereoisomers in high enantiomeric excess.



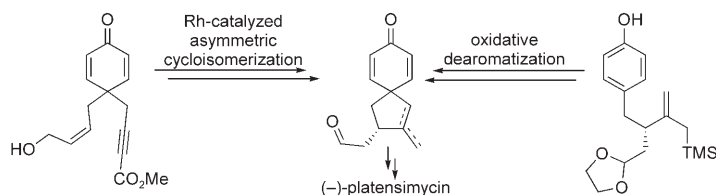
**IR operando** and “in situ” MAS NMR spectroscopic techniques were used to detect the intermediates involved in the carbonylation of methanol on zeolites (mordenite). The presence of Cu as well as Brønsted acid sites enhances the rate of carbonylation over that of the metal-free sample (which produces mainly acetic acid) by preferential adsorption of CO and dimethyl ether on Cu and leads mainly to methyl acetate.



## Carbonylation

T. Blasco, M. Boronat, P. Concepción, A. Corma,\* D. Law, J. A. Vidal-Moya \_\_\_\_\_ **3938–3941**

Carbonylation of Methanol on Metal–Acid Zeolites: Evidence for a Mechanism Involving a Multisite Active Center



**There are two ways about it:** One route to the potent antibiotic (–)-platensimycin used a catalytic asymmetric cycloisomerization and the other an auxiliary-controlled asymmetric alkylation to set the configuration at a key chiral center (see

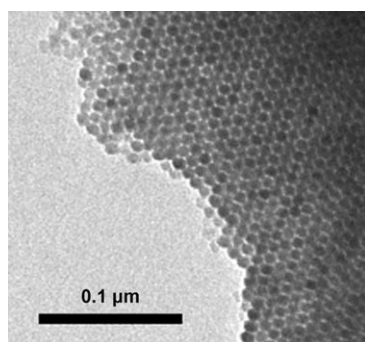
scheme, TMS = trimethylsilyl). This latter synthesis also used an oxidative dearomatization step to construct a key spirocyclic intermediate en route to the natural product.

## Natural Product Synthesis

K. C. Nicolaou,\* D. J. Edmonds, A. Li, G. S. Tria \_\_\_\_\_ **3942–3945**

Asymmetric Total Syntheses of Platensimycin

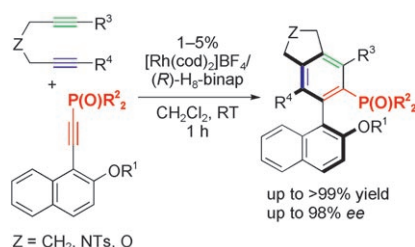
**Don't forget your coat!** Monodispersed  $\text{Mn}_3\text{O}_4$  nanoparticles, each encased in a thin shell of  $\text{MnO}_2$ , have been prepared for the first time. Ordered three-dimensional arrays of cubic symmetry were formed by self-assembly (see transmission electron microscope image). The nanoparticles exhibit strong interactions between the core and shell, resulting in spin-glass behavior.



## Ordered Nanoparticles

F. Jiao, A. Harrison, P. G. Bruce\* \_\_\_\_\_ **3946–3950**

Ordered Three-Dimensional Arrays of Monodispersed  $\text{Mn}_3\text{O}_4$  Nanoparticles with a Core–Shell Structure and Spin-Glass Behavior



**Densely substituted** title compounds can be obtained efficiently through an enantioselective [2+2+2] cycloaddition catalyzed by a cationic  $\text{Rh}^I/\text{H}_8\text{-binap}$  complex (see scheme). This method is highly practical in view of the ready access to substrates, mild reaction conditions, operational simplicity, and high catalytic activity. cod = 1,5-cyclooctadiene;  $\text{H}_8\text{-binap}$  = 2,2'-bis(diphenylphosphanyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl; Ts = *p*-toluenesulfonyl.

## Biaryl Synthesis

G. Nishida, K. Noguchi, M. Hirano, K. Tanaka\* \_\_\_\_\_ **3951–3954**

Asymmetric Assembly of Aromatic Rings To Produce Tetra-*ortho*-Substituted Axially Chiral Biaryl Phosphorus Compounds

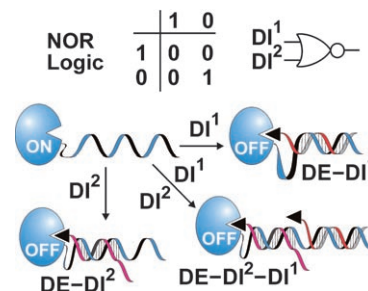


## Programmable Enzymes

N. C. Gianneschi,  
M. R. Ghadiri\* — 3955–3958

- Design of Molecular Logic Devices Based on a Programmable DNA-Regulated Semisynthetic Enzyme

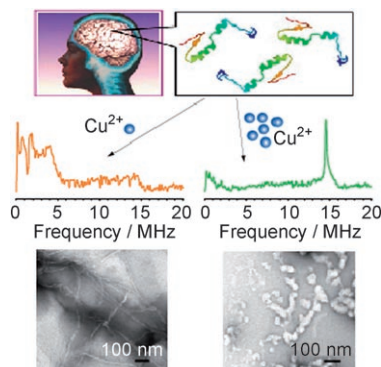
**Informed decisions:** Logic operations (AND, OR, NOR) can be performed with an enzyme by tagging it and its inhibitor with single-strand DNA. By adding appropriate single-strand DNA, the activity of the enzyme complex can be switched ON and OFF (see picture for NOR logic; **DE**: DNA-tagged enzyme; **DI<sup>1</sup>**, **DI<sup>2</sup>**: DNA-tagged inhibitors), or it can be used as a sensitive PCR-independent gene-diagnostic probe.



## Peptide Aggregation

S. Jun, S. Saxena\* — 3959–3961

- The Aggregated State of Amyloid- $\beta$  Peptide In Vitro Depends on  $\text{Cu}^{2+}$  Ion Concentration

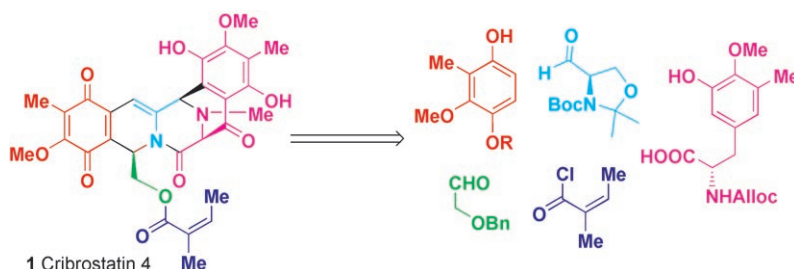


**Hold them or fold them:** The morphology of aggregated amyloid- $\beta$  depends on the concentration of  $\text{Cu}^{2+}$  ions, as shown in the TEM images. Distinct differences in the coordination of  $\text{Cu}^{2+}$  ions to amyloid- $\beta$  are observed by electron spin resonance as the metal concentration increases. The results suggest a correlation between specific  $\text{Cu}^{2+}$  ion coordination and the overall morphology of aggregates.

## Natural Products Synthesis

X. Chen, J. Zhu\* — 3962–3965

- Total Synthesis of the Marine Natural Product (–)-Cribrostatin 4 (Renieramycin H)



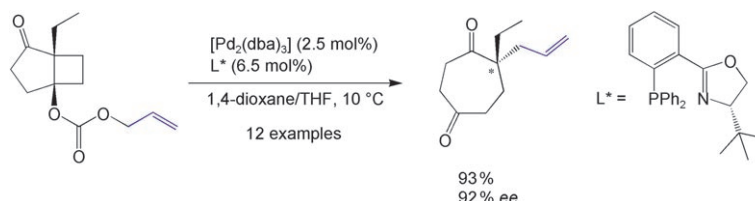
**Winning at dominoes:** The cytotoxic title compound was synthesized from five readily available starting materials in a longest linear sequence of 21 steps and 4.3% overall yield. The key step in the construction of the pentacyclic core of **1**

was a domino sequence involving  $\beta$  elimination and an intramolecular phenolic Mannich reaction. Alloc = allyloxycarbonyl, Bn = benzyl, Boc = *tert*-butoxycarbonyl.

## Asymmetric Catalysis

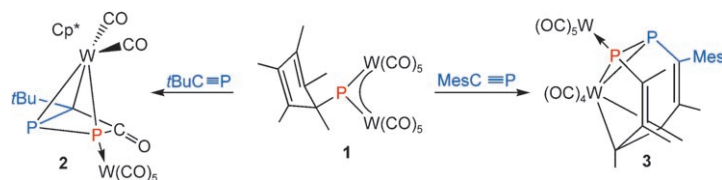
S. R. Schulz, S. Blechert\* — 3966–3970

- Palladium-Catalyzed Synthesis of Substituted Cycloheptane-1,4-diones by an Asymmetric Ring-Expanding Allylation (AREA)



**The right AREA:** Functionalized, seven- and eight-membered carbocycles are available from an asymmetric Pd-catalyzed decarboxylative fragmentation of strained bicyclo[3.2.0]heptane-2-ones (see

scheme, dba = *trans,trans*-dibenzylideneacetone). The products were formed in a sequence of [2+2] cycloaddition, retroaldol reaction, and asymmetric allylation of ketone enolates.



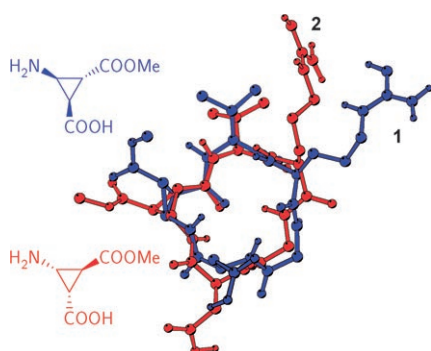
**Not as innocent as it looks:** Reaction of the phosphinidene complex **1** with  $t\text{BuC}\equiv\text{P}$  leads, via a  $\text{W}\equiv\text{P}$  triply bound intermediate, to the diphosphabutynonyl ligand complex **2**, whereas the reaction with  $\text{MesC}\equiv\text{P}$  ( $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ )

leads, through an unprecedented ring opening of the “innocent”  $\text{Cp}^*$  ligand ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ) and insertion of the phosphalkyne and the phosphinidene P atom, to the novel diphosphacyclooctatetraene ligand complex **3**.

### Phosphaalkyne Insertions

M. Scheer,\* D. Himmel, B. P. Johnson, C. Kuntz, M. Schiffer — 3971–3975

Ring Expansion of a  $\text{Cp}^*$  Moiety:  
Formation of a 1,2-Diphosphacyclooctatetraene Ligand



**Complete opposites:** The incorporation of the rigid building block (+)- $\beta\text{-Acc}$  ( $\text{Acc} = \text{aminocyclopropane carboxylic acid}$ ) into cyclic RGD peptides results in a high affinity towards the integrin  $\alpha_v\beta_3$ . The peptides **1** and **2** are composed of the enantiomeric building blocks (+)- (blue) and (-)- $\beta\text{-Acc}$  (red). The active peptide **1** inhibits integrin  $\alpha_v\beta_3$  mediated cell adhesion to vitronectin with an  $\text{IC}_{50}$  value of 20 nM.

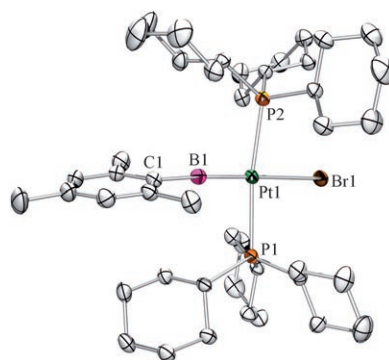
### Integrin Ligands

S. Urman, K. Gaus, Y. Yang, U. Strijowski, N. Sewald,\* S. De Pol, O. Reiser\* — 3976–3978

The Constrained Amino Acid  $\beta\text{-Acc}$  Confers Potency and Selectivity to Integrin Ligands



**Making a B line:** The boryl complex  $\text{trans}[(\text{Cy}_3\text{P})_2\text{Pt}(\text{Br})\{\text{B}(\text{Mes})\text{Br}\}]$  was synthesized and converted into the first two-coordinate borylene complex of platinum,  $\text{trans}[(\text{Cy}_3\text{P})_2\text{Pt}(\text{Br})(\text{BMes})]^+$  (see picture), in which the boron atom is linearly coordinated. The bonding situation was analyzed by theoretical calculations and structural methods.  $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ .



### Boron Ligands

H. Braunschweig,\* K. Radacki, K. Uttinger — 3979–3982

Synthesis and Structure of a Cationic Platinum Borylene Complex



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



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

The issues for May 2007 appeared online on the following dates  
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